# THERMAL DEGRADATION OF POLYVINYL CHLORIDE

A thesis submitted to the University of Glasgow in accordance with the regulations for the award of the degree of DOCTOR OF PHILSOSPHY

by

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May, 1965.



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# Thermal degradation of polyvinylchloride.


## Summary.

The thermal degradation of polyvinylchloride has been investigated by several workers, and different mechanisms have been suggested for the degradation.

In the thermal degradation of PVC, hydrochloric acid is evolved and a coloured residue is left. In the present work, the problem was tackled in four different ways. The main aim was to assign a definite mechanism for the degradation. Commercial polymer prepared by suspension method, Geon 111 (JUB-49) was used for these measurements.

The influence of solvents on the degradation was investigated by carrying out the dehydrochlorination in presence of different solvents. The acid evolved was estimated by titrating it against standard caustic soda solution. The solvents used were, benzophenone, dioctylphthalate, dichloronaphthalene, benzyl alcohol, tritoluylphosphate and ethyl benzoate. It was observed that solvents have an influence on the dehydrochlorination, the rate being greatest in benzophenone and tritoluylphosphate.

A attempt has been made to explain these effects. The activation energy in the temperature range 187-243°C was also determined in the various solvents, and the values varied from 17.4 K.Cal $mole^{-1}$ in ethyl benzoate to 31.15 K.Cal $mole^{-1}$ in tritoluylphosphate.

The liberation of hydrochloric acid is accompanied by the introduction of a double bond in the polymer molecule. Successive production of double bonds leads to a long conjugated chain which causes a discolouration of the polymer. As no one had reported absorption studies on thermally degradaded polymer, such work was undertaken and forms part of this thesis.

The degradation was carried in presence of different solvents. The absorption studies indicated the existence of several bands in the ultraviolet and visible region. Such absorption spectra have been reported for conjugated polyenes. This work also revealed that the polymer species had the maximum number of double bonds corresponding to a value of 13 double bonds. However, a preferential production of polyenes having 2,3,4, 5 or 6 double bond takes place. The absorption spectra for most of the degraded polymer solutions (dichloronaphthalene, dioctylphthalate, tritolyl phosphate, benzophenone, benzyl alcohol, ethyl benzoate, nitrobenzene) were similar, but a different type of absorption pattern was obtained for dimethylformamide or acrylamide. A reaction scheme to account this has been suggested.

The effect of storage of a degraded polymer solution in vacuum and in presence of air has also been investigated. The influence of temperature on the absorption spectra was investigat using dioctylphthalate as solvent. At high temperatures, few long chain polyenes are produced and this is perhaps due to scissi of the polyene chain.

It has been argued that the degradation of a polymer molecul begins at some weak site in the molecule. The carbon carbon double bonds situated at the chain ends have so far been regarded as the primary source of initiation. To investigate this, commercial polymer was fractionated, and the discoloration and dehydrochlorination studies were performed on the fractions. The rate of dehydrochlorination and discoloration was independent of molecular weight. The phenomenon is explained by a sort of balance between carbon carbon double bonds situated at chain ends and tertiary chlorides resulting by branching of the polymer. Another interesting feature which emerged as a result of these fractionation studies was that the low molecular weight polymer was more crystalline (syndiotactic) than the high molecular weigh polymer.

Chain scission and cross linking are the two dher possible reactions in the thermal degradation of PVC. The changes in molecular weight of PVC during degradation were studied by light scattering measurements in cyclohexanone. These results indicated that an initial chain scission occurs to some extent, but later on cross-linking dominates.

The Ultracentrifuge measurements on PVC fractions indicated the existence of association in a few samples. This was also indicated by the light scattering measurements. 10 minutes heating at 178°C is sufficient to disintegrate the gel (as shown by the schlieren diagram). The degradation of polymer was also followed to some extent by ultracentrifuge. After 30 minutes of degradation a series of peaks are formed which sediment at different rates. This means that several polymeric species are produced as a result of degradation (or cross-linking).

The molecular weights of few of the fractions were also investigated by light scattering. The number average and weight average molecularе weights were determined from the Zimm plots and the constants of Mark-Houwink equation were evaluated. The value of second virial coefficients was high, showing that cyclohexanone is a good solvent for PVC.

ACKNOWLEDGEMENTS

The authoress wishes to express her sincere thanks to Dr. W.I. Bengough for his help and encouragement during the course of this work. Thanks are also due to Professor P.D. Ritchie, for providing facilities for carrying out this work, and to Distillers Company Ltd., for the award of a Research Studentship.

CONTENTS

Glossary of principal symbols used in the thesis

| | | |
|---|---|---|
| $C$ | = | concentration (in $gm.l^{-1}$ or monomoles $l^{-1}$) |
| $[\eta]$ | = | intrinsic viscosity ($dl.gm.^{-1}$) |
| $W_x$ | = | integral weight distribution function |
| $\gamma'$ | = | volume fraction of precipitant added to produce the first haze. |
| $\lambda''$ | = | logarithmic viscosity number |
| $\lambda''_o$ | = | limiting viscosity number |
| $k'_1$ and $\beta$ | = | constants, characteristic of given solute solvent system |
| | = | dielectric constant of solvents |
| $\frac{dHCl}{dt}$ | = | rate of dehydrochlorination (moles of acid $l^{-1}sec.^{-1}$) |
| $k'$ | = | rate constant ($sec.^{-1}$) |
| $\lambda, \lambda_o$ | = | wavelength |
| $n$ | = | number of double bonds |
| R.H. | = | relative height of peaks with reference to absorption peak at 364 m u |
| THF | = | tetrahydrofuran |
| DMF | = | dimethylformamide |
| DOP | = | dioctylphthalate |
| TTP | = | tritoluylphosphate |
| MeOH | = | methyl alcohol |
| K and $\alpha$ | = | constant of Mark Houwink equation |
| $\bar{M}$ | = | viscosity average molecular weight |
| $\bar{M}_z$ | = | Z-average molecular weight |

$\bar{M}_w$ = weight average molecular weight

$\bar{M}_n$ = number average molecular weight

$\partial\eta/\partial c$ = refractive index increment

$I_o$ = intensity of scatter for solvent

$I$ = intensity of scatter for solution

$I_s$ = $(I-I_o) \times \frac{\sin\theta}{1+\cos^2\theta}$

$k_1$ = arbitrary constant

$P_\theta$ = particle scattering factor

$B$ = second virial coefficient

$R_\theta$ = measured Rayleigh ratio at an angle $\theta$ to incident beam.

no = refractive index of benzene

NA = Avogadro's number

$I_B$ = intensity of light scattered at 90° by standard benzene

$\langle\bar{\rho}\rangle_z$ = radius of gyration

$\langle\bar{r}\rangle_z$ = Z-average mean square end to end distance

$\lambda'$ = $\frac{\text{Wavelength of light in vacuum}}{\text{refractive index of solution}}$

$l$ = intensity of light transmitted

$l_o$ = intensity of incident light

$d$ = path length of light

$\alpha$ = extinction coefficient

$S_c$ = sedimentation coefficient

$\omega$ = angular velocity

| | | |
|---|---|---|
| $x$ | = | distance between particle and centre of rotation |
| $t$ | = | time (in minutes) |
| r.p.m. | = | rotations per minute |
| $\frac{1}{M_A}$ | = | magnification factor |
| $F_1 - F_9$ | = | fractions of PVC obtained by using THF/water system |
| $b_1 - b_2$ | = | fractions of PVC showing association (prepared from THF/water system) |
| $K_1$, $K_2$ | = | Constants. |

# CHAPTER 1

## Introduction

Polyvinylchloride and its various copolymers are used not only for domestic purposes, but also in products of growing industrial importance. Its applications are, however, limited by the stability of the polymer during processing. The problem is of great industrial importance, because the initial degradation at the time of processing causes a modification of the properties of final product e.g. colour (which changes from colourless to yellow, reddish brown, red and finally black), mechanical properties, and electrical characteristics.

The thermal degradation of polyvinylchloride has been investigated by several research workers. The breakdown of the polymer is very complicated and several mechanisms have been suggested. Still the problem is by no means solved. There are two prevalent views regarding the mechanism of degradation namely molecular elimination of hydrochloric acid and a free radical mechanism.

In the present investigations, the problem was tackled in four different ways. The overall aim was to assign a definite mechanism for the degradation and to study the structural changes taking place in the polymer chain.

In the first approach the polymer was degraded in solvents

and the rate of dehydrochlorination was followed by titration. Degradation in solution enables us to determine the dependence of the rate on the polymer concentration. It also facilitates the diffusion of the evolved gases which might otherwise be partially trapped in the polymer. Several solvents were used in this particular work. Bengough and Sharpe[9] degraded polyvinyl-chloride in ethyl benzoate, nitrobenzene and o.dichlorobenzene. However, the main work was done using ethyl benzoate, as they found that nitrobenzene attacked the polymer, while o.dichlorobenzene which had a lower boiling point (182°C) could not be used for the degradations work (as the temperature range was 178-212°C). The precise purpose of our study using different solvents was to investigate the influence of solvents on the breakdown of the polymer. It was observed that solvents do have an effect on the dehydrochlorination of polyvinylchloride. The activation energy for dehydrochlorination varied from solvent to solvent. The solvents could be divided into three groups on the basis of their activation energy. Benzophenone and tritoluyl phosphate (activation energy 30.6 and 31.1 k. cal./mole) could be grouped together, while dichloronaphthalene (24.2 k.cal./mole), dioctyl phthalate (21.1 k.cal./mole) and benzyl alcohol (23.03 k. cal./mole) formed the second group. Ethyl benzoate had the lowest activation energy and belonged to the third group. A first order dependence of rate on polymer concentration was observed, but a variation of ($\pm$ 0.2)

from this value was found. This may be due to variation in the mechanism at higher temperatures.

Another approach to the problem was to follow the colour changes occuring during degradation using an ultraviolet spectrophotometer. Absorption studies, of polymer degraded under the influence of ionising radiations have been made by several workers, but so far this method has not been applied to thermally degraded polymer. Atchison[35] has reported the formation of a broad absorption band in the visible region, with fine peaks superimposed on it.

Our results using ultraviolet spectrophotometer, showed the presence of several absorption peaks in the polyvinylchloride degraded at 198°C in various solvents. Another interesting observation was that polyene chain having 6 or 7 double bonds were formed in higher proportion than those having 10 or more double bonds. Storage of a degraded solution of polyvinylchloride under vacuum at room temperature, caused an increase in the absorption, indicating that dehydrochlorination may proceed to some extent even at room temperature.

It has been argued that the dehydrochlorination starts from some weak points in the polymer chain. Carbon carbon double bonds situated at chain ends are perhaps the weak points. The rate of dehydrochlorination (and consequently absorption) therefore, should vary inversely with the molecular weight of the polyvinylchloride.

The polymer was therefore fractionated and absorption studies were performed on the degraded fractions in solution. The U.V. measurements indicated that the formation of colour was independent from molecular weight.

Chain scission and cross-linking are the two other possible reactions that may take place during degradation. An attempt was made to follow the molecular weight changes taking place during degradation, using light scattering and ultracentrifuge techniques. Our experiments using light scattering technique did not prove to be as useful as was hoped. The degradation of polymer imparted a colour to the solution which made the measurements for light scattering a bit difficult. Zimm plots became very much twisted after 30 minutes of degradation. Chain scission to a certain extent takes place initially, but later on cross-linking dominates.

Molecular weights of few of polyvinylchloride fractions were also determined using light scattering technique, and thus the constants of Mark Houwink equation were evaluated.

## Degradation of polymers in general

The term degradation when used in connection with macromolecules indicates some sort of physical deterioration accompanied by chemical change in the molecule. It does not, necessarily mean, a lowering of molecular weight which on the contrary may increase in some cases.

This degradation of polymers may be brought about by physical (heat, light) or chemical means (oxidation, hydrolysis). Structural abnormalities (as branches or double bonds situated at chain ends) usually initiate the degradation by physical agencies, which then continues by a series of chain reactions. The role of structural abnormalities may be less important in the case of chemically induced reactions. Here the reagent attacks at some structure characteristic of the monomer units.

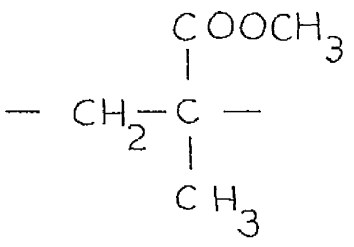
Out of these two possible ways of polymer degradation, only the degradation brought under the influence of physical agencies will be considered in this thesis.

Heat is the most generally applicable means for the degradation of polymers and has been extensively investigated. The thermal degradation of polymers may involve either (a) chain scission reactions or (b) non-chain scission reactions. These two will be discussed separately.

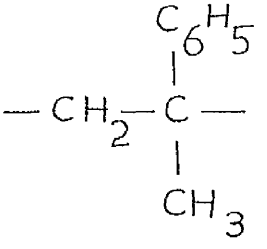
(a) Chain scission reactions - Here scission of the main polymer chain takes place. This process may be either a systematic

scission (depolymerisation) or a random scission.

Depolymerisation - This process is reverse of polymerisation and monomer is produced in high yields. Depolymerisation proceeds by a free radical mechanism. Grassie[1] has suggested that compounds having quaternary carbon atoms usually produce large amounts of monomers (unsaturated polymers as natural rubber is an exceptions):



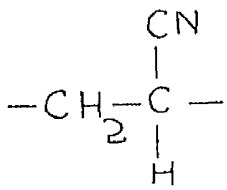
Polymethyl methacrylate



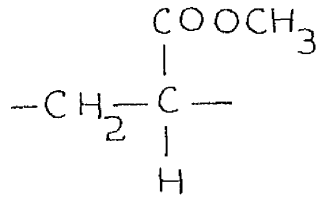
α-methyl styrene

Methacrylonitrile and vinylidene cyanide etc. belong to this group. The polymers which generally degrade to give monomers, have a low heat of polymerisation (10 - 13 k.cal./mole).

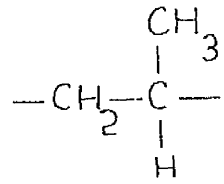
Random chain scission - Here the polymer is split in fragments which in general contain a number of monomer units. The replacement of a substituent of a quaternary carbon atom by hydrogen atom decreases the monomer yield. The heat of polymerisation of such polymers is also high (about 20 k.cal./mole).



Acrylonitrile



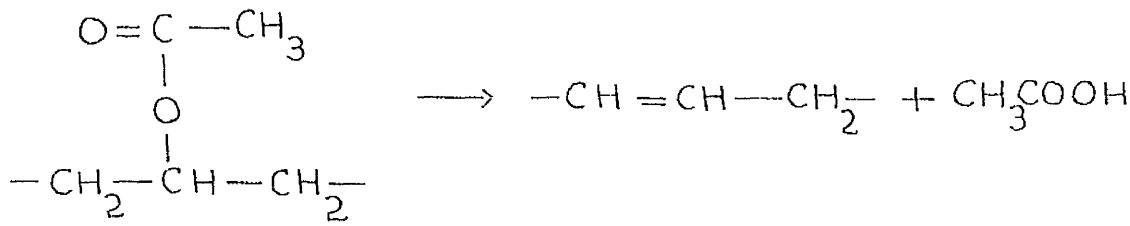
methyl acrylate



propylene

Non-chain scission reactions - Here the polymer chain remains intact and a modification of the substituent takes place. This modification may be manifested by the elimination of side groups (as acids in case of polyvinyl esters) or by the formation of cross links.

The volatile product formed in the decomposition of vinyl esters is usually the corresponding acid e.g.

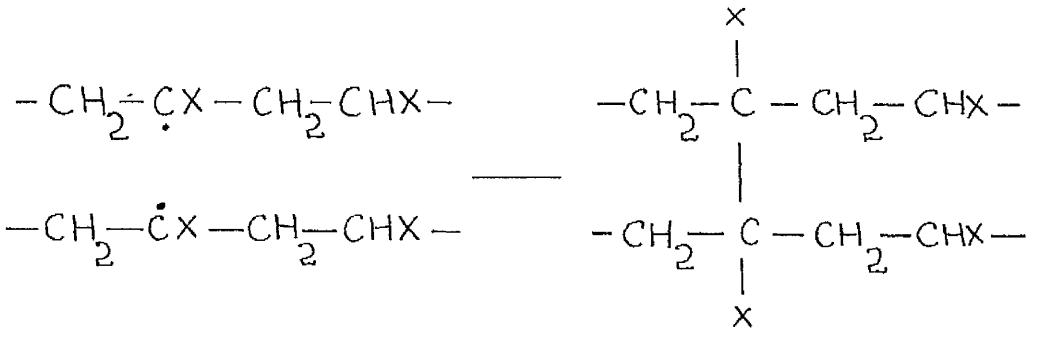


Polyvinylacetate

Polyvinylchloride and polyvinylidene chloride are the other examples.

This type of reaction may occur to a measurable extent at temperatures as low as 160 - 180°C.

In the cross-linking reaction, a polymer network may be obtained by the combination of polymer radicals or molecules during the course of degradation.



This in general is a brief outline of the various possible reactions, which may take place during course of degradation.

## Thermal degradation of polyvinylchloride

### Previous Work

The thermal degradation of polyvinylchloride (PVC) (as encountered during processing) leads to the liberation of hydrochloric acid. This leads to the formation of a reddish brown polymer for which a polyene structure has been assigned[2]. This polyene residue may well result from the splitting out of chlorine atoms together with adjacent hydrogen atoms. Before going into the details of the mechanism of degradation, it would be better first to consider the structure of PVC.

Structure of PVC. It has been established by the chemical analysis[2,3], X-ray studies etc. that PVC has a regular head-to-tail arrangement $-CH_2CHClCH_2CHClCH_2CHCl-$ and not an alternating head-to-head tail-to-tail $-CH_2CHClCHClCH_2CH_2CHCl-$ structure. The polar nature of the double bond is perhaps responsible for the head-to-tail arrangement ($CH_2=\overset{+}{C}H\rightarrow\bar{C}l$). However, the presence of even a small amount of irregular structure might have important ramifications. Further, the presence of two adjacent substituent atoms (e.g. chlorine) might offer a point of inherent weakness in the polymer chain, as observed in polyvinylalcohol.[4]

The presence of tertiary chlorides in PVC has been shown by the work of Cotman[5]. He converted PVC into a hydrocarbon by hydrogenation and then estimated the branch content by measuring

the infrared absorption of the methyl group. His result indicated a branch content of 20 per molecule. These branches are formed during polymerisation, either by a chain transfer between a growing radical and an already formed polymer molecule or by back-biting. The work of Kharasch et. al.[6] with diacetyl peroxide and various chloroalkanes indicated that chain transfer reaction most likely take place with the hydrogen on the same carbon as chlorine. This evidence led Baum and Hartman[11] to believe that most of the branches in PVC are attached to the chain in a tertiary chloride type structure. (However, as would be pointed out later, other works on PVC indicate that $-CH_2-$ groups are more prone to free radical attack than -CHCl groups). Back-biting would also introduce branching.

$$\sim\sim CH_2CHClCH_2CHClCH_2\dot{C}HCl. \longrightarrow \sim\sim\dot{C}HCHClCH_2CHClCH_2CH_2Cl$$

Branching of ($\sim\sim CH_2CHClCH_2\dot{C}HCH_2CHCl\sim\sim$) this type can also be introduced by a chlorine transfer.

Carbon-carbon double bonds are present at the chain ends of the polymer. These may be formed either by a chain transfer reaction with the monomer or by disproportionation. The former is believed to be the main reaction[7], and this introduces a β-chloro unsaturated structure.

$$\sim\sim\sim CH_2\dot{C}HCl + CH_2 = CHCl \longrightarrow \sim\sim CH = CHCl + CH_3\dot{C}HCl$$

Chain ends may also have the foreign groups, such as the catalyst fragments which are incorporated in during the polymerisation ($R.+H \longrightarrow RH$. where R. may be a radical formed from acyl peroxide, persulphate or inorganic persalt etc.)

Mechanism of PVC degradation

The investigations of previous workers have indicated that pyrolysis of the polymer proceeds by the elimination of side groups i.e. dehydrochlorination. This may be defined as a process of removing HCl from a molecule with the introduction of a double bond into the system.

$$-CH_2CHClCH_2CHCl- \longrightarrow -CH=CHCH_2CHCl- + HCl$$

The dehydrochlorination of PVC is influenced by the atmosphere in which it is carried out (i.e. inert atmosphere or in presence of oxygen). The degradation in presence of nitrogen will be discussed first followed by a discussion on the degradation in presence of oxygen.

Dehydrochlorination in nitrogen

As has already been mentioned in the introduction, the dehydrochlorination of PVC has been explained by (a) molecular elimination of HCl and (b) a free radical reaction.

Since there is a significant difference between the two mechanisms these will be discussed separately.

(a) Molecular elimination of HCl

The terminal polymer groups, especially the double bonds, probably constitute the majority of initial weak sites, and are thus responsible for the instability of the polymer. Omoto and Otsu[8], Bengough and Sharpe[9] noted poor heat stability of low molecular weight products. Similarly Talamini and Pezzin[10] using the fractions of PVC observed that the rate of dehydrochlorination was inversely proportional to the molecular weight of PVC. A lowering of the rate of dehydrochlorination has been reported for chlorinated PVC[11] (which would have no double bonds). It has also been observed[10] that the rate of dehydrochlorination could be increased tremendously by the deliberate introduction of carbon carbon double bonds. These facts substantiate the view that terminal polymer groups are responsible for the initiation of dehydrochlorination. However, one should not be misled by the above discussion, because it is still not certain which weak points in the polymer structure are responsible for the onset of degradation. In their recent publication, Talamini et. al.[12] have reported that the terminal groups unless present in a high percentage do not affect the degradation of polymer.

Tertiary chlorides also appear to initiate dehydrochlorination, particularly at later stages of degradation[11]. Asahina

and Onozuka[13], working on gaseous pyrolysis of chain end model compounds of PVC, have concluded that allyl type chlorine and tertiary chlorine in main chain of polymer are the weak points.

Once a molecule of acid is lost an allylic chloride exists, in which the chlorine atom remaining on the polymer chain is quite unstable through the activation on neighbouring double bonds. This facilitates the liberation of another HCl molecule. Succeeding molecules of acid are lost down the chain in a 'Zipper' fashion.

$$-CH_2CHClCH_2- \longrightarrow HCl + -CH=CH-CH_2-CHCl-$$

$$-CH=CH-CH_2CHCl \longrightarrow HCl + -CH=CH-CH=CH-$$

This dehydrochlorination thus leads to an extensive conjugation [R $(CH=CH-CH=CH)_n$-] which is responsible for the discolouration of PVC. Lewis and Calvin[14] have suggested that a minimum of 7 conjugated double bonds is essential for the production of colour.

Termination of the reaction is believed to take place when it runs into a change in structure of the polymer chain. This could be caused either by oxidation or chain branching.

Baum and Wartman[11], Grassie[15] and Druesedow and Gibbs[22] have supported this molecular elimination of HCl.

Free radical mechanism for the degradation of PVC

Arlman[16] was the first to suggest a free radical mechanism

for the degradation of PVC. Like most of the free radical reactions, an initiation, propagation and termination steps have been suggested.

According to Arlman, the reaction starts by the thermal splitting off, of terminal end groups, and thus giving rise to two radicals.

$$RCH_2CHClCH_2CHCl- \longrightarrow R\cdot + \cdot CH_2CHClCH_2CHCl-$$

This introduces an unstability in the molecule and causes the liberation of HCl. The various reactions, according to his scheme could be represented as follows.

$$\cdot CH_2CHClCH_2CHClCH_2- \longrightarrow HCl + \cdot CH_2CH=CHCHClCH_2-$$

$$\cdot CH_2CH=CHCHClCH_2- \rightleftharpoons CH_2 = \dot{C}HCHCHClCH_2-$$

$$CH_2=\dot{C}HCHClCH_2 \longrightarrow CH_2 = \dot{C}HCH=CH- + HCl$$

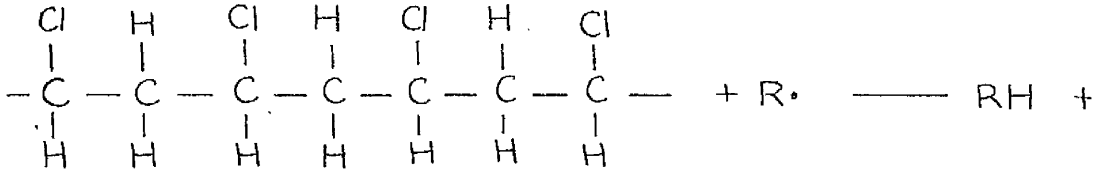
$$CH_2=CH\dot{C}HCH=CH- \rightleftharpoons CH_2 = CH\dot{C}H=CH-$$

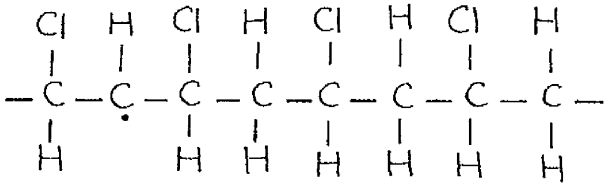
$$CH_2=CHCH=CH\dot{C}HCHClCH_2 \longrightarrow CH_2 = CHCH=CH\dot{C}HCH=CH-$$

$$CH_2=CHCH=CH\dot{C}HCH=CH- \rightleftharpoons CH_2 = CHCH=CHCH=C\dot{H}-$$

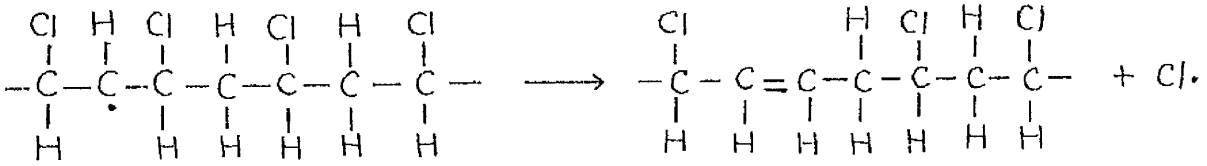
Winkler[17] in a review paper suggested a free radical mechanism for the evolution of HCl by PVC, as Barton and Howlett[18] have proposed for 1,2 dichloroethane. The initiating radicals could come from the catalyst residue left from the polymerisation process, or they could arise as a result of oxidation. Fuchs and Wilis[19] chlorinated PVC (which is supposed to be a free radical reaction) and observed that $-CH_2-$ groups of the polymer are

attacked. Drawing an analogy with this reaction, Winkler suggested that the initiating radicals attack the methylene hydrogen atoms preferentially.

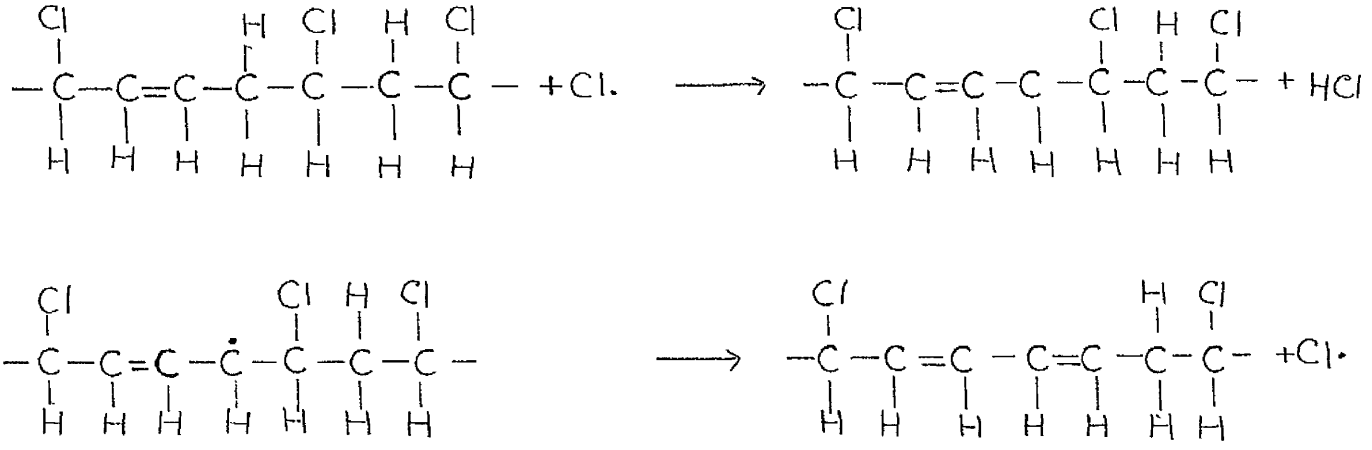




This would make the chlorine atom in β position labile, which would then be released to stabilise the molecule.



This chlorine atom, attacks the hydrogen atom from one of the nearest methylene groups. Since this is also an allylic hydrogen its abstraction is highly favoured. Thus a chain reaction is started and perpetuated which could lead to a conjugated structure.



The above chain could possibly continue until a very long polyene system develops.

Termination of the chain in a particular molecule could result if -

a) the chlorine atom abstracted a hydrogen atom from a carbon atom attached to a chlorine .

b) the chlorine atom abstracted hydrogen atom from another molecule.

c) PVC radical reacted with oxygen (if present).

d) the PVC radical or the chlorine atom reacted with another radical as

$$R\cdot + Cl\cdot \longrightarrow P \quad \text{or} \quad Cl\cdot + Cl\cdot \longrightarrow Cl_2 \quad \text{or} \quad R\cdot + R' \longrightarrow P'$$

The reaction a,b and c will stop the growth of a particular chain but they may be capable of starting new chains and are really chain transfer reactions.

Kinetic measurements by Stromberg and coworkers[20] gave a

rate dependence on polymer concentration of 3/2. This he claims favours a free radical mechanism for degradation. The decomposition was however, taken to 50% conversion. The polymer at this stage bears little resemblance to the original polymer. It is, therefore, doubtful whether these results have any significance regarding the decomposition of original polymer.

Talamini and Pezzin,[10] and Guyot et. al.[21] support Winkler's mechanism for degradation. Bengough and Sharpe[9] used free radical initiators to initiate dehydrochlorination at temperatures which are below the normal degradation temperatures (100°C, 130°C and 150°C). There was an insignificant effect on the rate of dehydrochlorination at these temperature. This means that the activation energy for the propagation reaction is not very different from that for the initiation reaction, which is generally not the case in free radical chain processes. They have suggested dehydrochlorination as a free radical raction, but not a chain reaction.

$$CHCl = CHCHClCH_2CHCl \longrightarrow CHCl = C\dot{H}CHCH_2CHCl- \quad (+Cl\cdot)$$

$$CHCl = C\dot{H}CHCH_2CHCl- \quad (+Cl\cdot) \longrightarrow HCl + CHCl = CHCH=CHCHCl-$$

Any mechanism for degradation must also explain cross linking and chain scission, the two reactions which are known to occur.

There is an increase in the intrinsic viscosity of the polymer with increasing heating time and this is attributed to cross linking[11,22]. **Druesedow** and Gibbs[22] have offered the following four mechanism for cross linking.

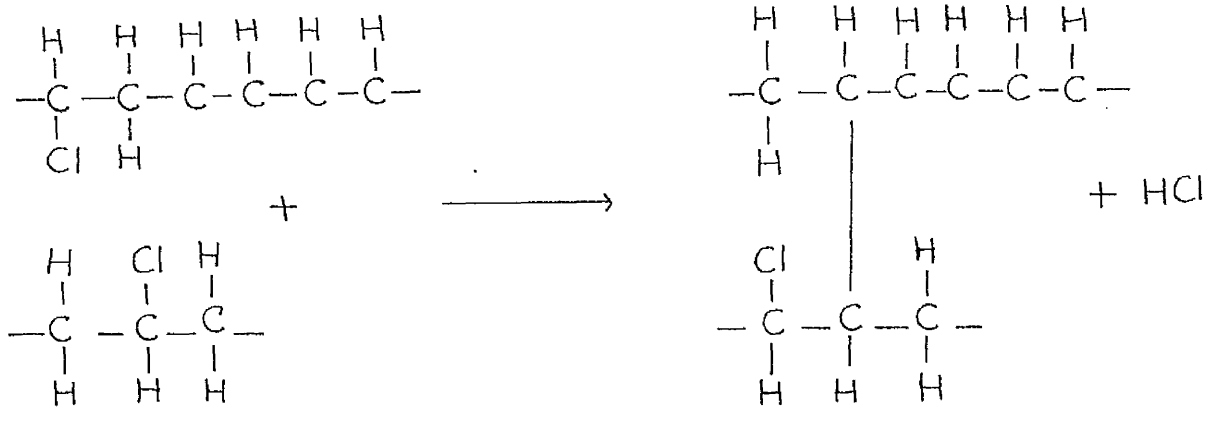
(1) Copolymerisation between polyene groups.

(2) Chain transfer between a polyene group and a segment of a normal polymer chain.

(3) A Diels Alder reaction.

(4) Cross dehydrochlorination between a point of high chlorine activity on one chain and hydrogen atom on another.

These authors favoured the mechanism of cross dehydrochlorination.



Bengough and Sharpe[24] also support this view of intermolecular condensation with the elimination of HCl.

Winkler[17] has suggested the following free radical mechanism for cross-linking.

A polymer radical adds to the conjugated unsaturation of another chain.

The resulting radical could stabilise itself by

a) Abstracting hydrogen atom from another molecule.

b) Loosing a hydrogen atom from the radical resulting in the formation of a double bond.

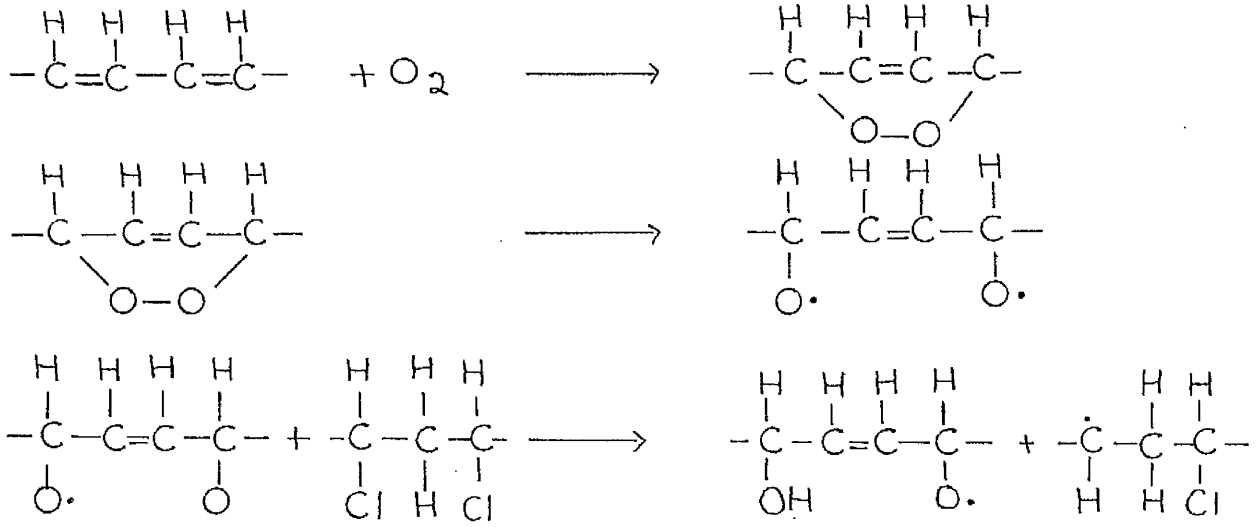
c) Forming an alkyl peroxy ($RO_2$) radical in presence of oxygen.

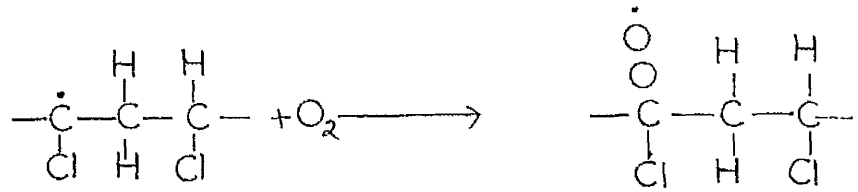
Chain scission is noticeable in early stages of degradation where a lowering in intrinsic viscosity is observed. Taylor[23] has demonstrated that cross-linking and chain scission occur simultaneously, by determining the solubilities and intrinsic viscosities of samples of degraded PVC.

## Degradation in presence of oxygen

Hydrogen chloride is evolved at a higher rate in presence of oxygen than in presence of nitrogen[11,16,22]. Furthermore there is an acceleration in rate with degradation time. Boyer[25] and Fox[26] have shown that carbonyl groups are formed, which indicates that an oxidation of the polymer chain has taken place. Weak points in PVC such as the tertiary hydrogen atoms are vulnerable to oxidative attack.

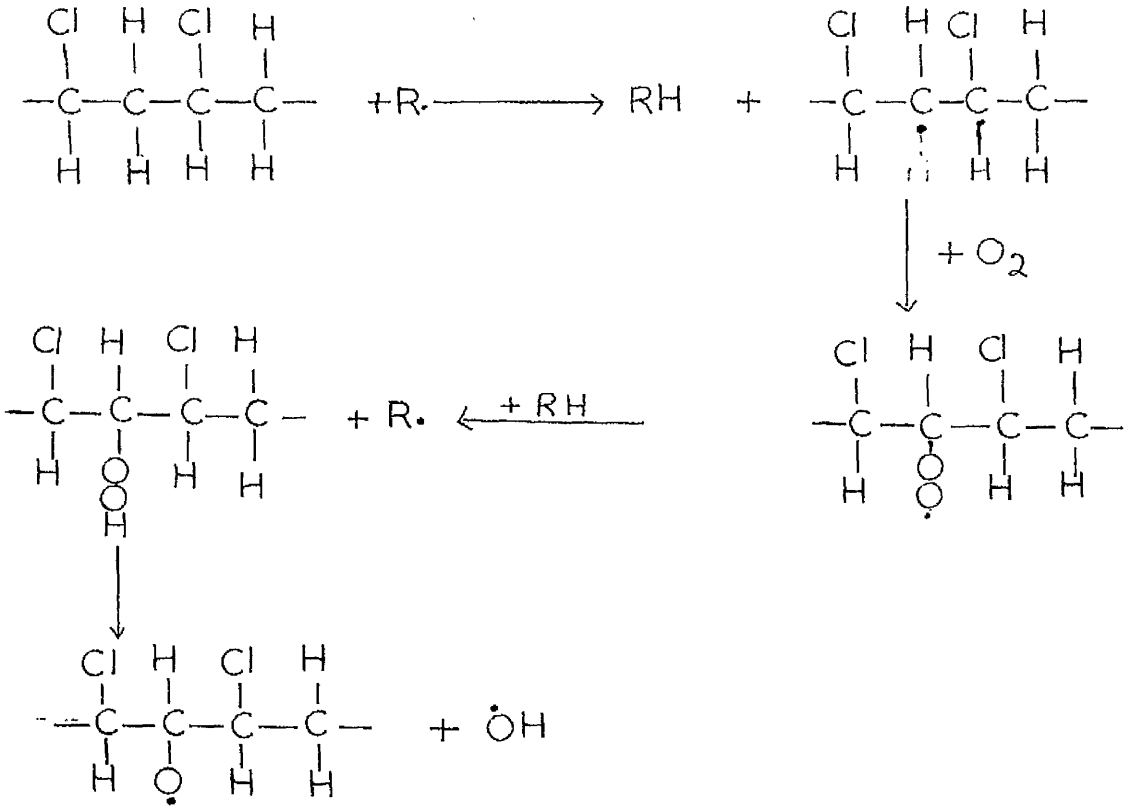
Polymer degraded in bulk in presence of oxygen is less coloured than degraded in its absence[16,22]. This suggests that oxygen reacts with unsaturated groups. Oxidation almost certainly proceeds by a free radical mechanism. Oxidative initiation, commencing within the polymer chain is perhaps responsible for the acceleration of rate in presence of oxygen.

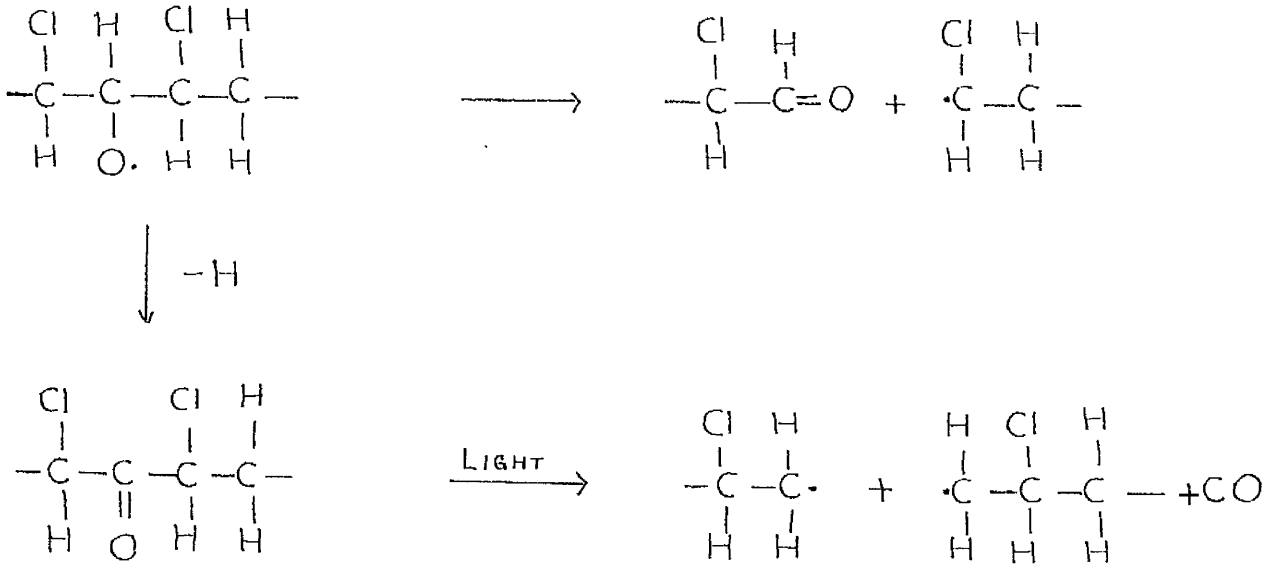




Thus peroxy radicals and alkoxy radicals are formed by a reaction with $O_2$, and this also accounts for the presence of oxygen. However, it has been noted[9] that polymer degraded in a solution in an oxygen atmosphere darkened much rapidly than in nitrogen and there was no significant difference in the rates of dehydrochlorination.

A decrease in the initial viscosity of the polymer takes place during the degradation in presence of oxygen[22]. Because of the formation of peroxide the polymer is more likely to undergo chain scission. The following mechanism has been proposed for chain scission[14].






The formation of peroxide radicals in presence of oxygen has also been supported by Campbell and Rauscher[27].

Influence of temperature on degradation

Most of the work on the thermal degradation of PVC has been done at the temperatures generally existing during processing (100°C - 200°C). Bradt and Mehler[28], however, studied the degradation upto 300°C and observed that HCl was the main product. Stromberg et. al.[20] studied the decomposition of and benzoyl peroxide initiated PVC at 300°C and observed that the main product was HCl together with some benzene. This latter would be formed if the conjugated chain were to cyclize into a stable six membered ring, with the subsequent breaking of the weakened

bond α to the ring. A 30 minutes thermal treatment at this temperature removed all HCl and a secondary pyrolysis of this dehydrochlorinated PVC yielded low molecular weight saturated and unsaturated hydrocarbon, by apparantly a random chain cleavage.

The Photodegradation of PVC

Polyvinylchloride is stable for years in dark, but degrades in sunlight. The degradation of polymer is enhanced by subjecting it to U.V. irradiation.

Scarbrough[29] believed that the U.V. light catalyzed the reaction after a short induction period. Mack[30] suggested that after the initial dehydrochlorination, oxidation of the chain takes place. Thus the effect of light and oxygen appears to be interdependent.

Winkler[17] has suggested a radical mechanism for the photo-degradation of PVC, similar to the one discussed for the thermal degradation.

Chain scission and cross linking of the polymer may take place when it is exposed to U.V. light at room temperature[23].

The electronic irradiation of PVC

When PVC is subjected to a beam of high energy electrons at low temperatures, a visible colour change takes place. Lawton and collaborators[31] investigated the effect of high energy electrons on several polymers and observed that PVC degrades on

irradiation. Chapiro[32] investigated this radiolysis of PVC in the solid state in great detail. He observed that PVC films irradiated in oxygen were less coloured than the films degraded in vacuum. To account for the colour, he suggested the existence of 'frozen in' free radicals together with the polyene chains. Miller[33] explained the radiation and post irradiation effects observed for PVC on basis of a free radical chain dehydrochlorination reaction, a mechanism similar to that of Winkler[17]. The primary free radical process in the radiolysis of PVC is

$$-CH_2CHCl- \longrightarrow CH_2\dot{C}H + Cl. \qquad (1)$$

This process may occur even at -190°C but the radicals remain trapped. On warming to room temperature, free radical reactions of the following type take place.

$$Cl. + CH_2CHCl- \longrightarrow HCl + -\dot{C}HCHCl- \qquad (2)$$

$$-\dot{C}HCHCl- \longrightarrow -CH=CH- + Cl. \qquad (3)$$

$$Cl. + -CH=CHCH_2CHCl \longrightarrow -CH=CH\dot{C}HCHCl \qquad (4)$$

Miller also suggested that propagation may not involve a free chlorine atom but rather a simultaneous dissociation and abstraction.

Atchison[34,35] and Loy[36] by E.S.R. and optical measurements have shown the existence of three types of radicals in PVC by ionising radiations. These three types of radicals (short, intermediate and long lived radicals) decay exponentially with time and have half lives of 54 mins., 720 mins. and 3200 hrs. respectively at 30°C. Atchison also observed that the concentration of colour producing material was inversely proportional

to the concentration of long lived radicals, a finding similar to that of Lawton and Balwit[37]. Ohnishi et. al.[38] observed an increase of longer conjugated system on storage. These workers support Miller's mechanism of degradation. Cross linking as induced by radiation has also been investigated.

Stabilisation of PVC

Early workers[26] believed that dehydrochlorination was auto-catalysed by hydrochloric acid. Most of the stabilisers used, therefore were acid acceptors such as metal soap stabilisers. Their action was explained in two ways.

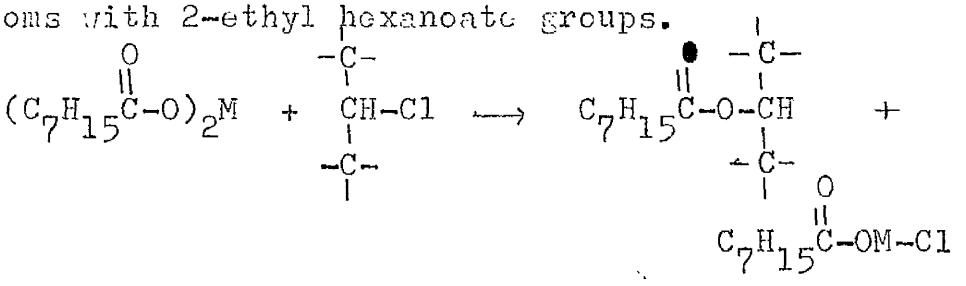
(1) By double decomposition as the reaction of a weak acid salt with HCl with the formation of metallic chlorides e.g. calcium stearate etc. The metal salt portion may be Ca, Ba, Cd, Sr, Pb or Sn whereas the organic acid part could be a saturated fatty acid ( stearic and lauric) an unsaturated fatty acid (ricinoleic acid or maleic acid) an aromatic acid (salicylic acid) .

(2) By addition as in case of epoxy derivatives or amines to form stable hydrochlorides

The more recent evidence[22,39], however, indicates that autocatalysis may occur only in certain atmospheres. Arlman[16] passed a stream of HCl gas over PVC during pyrolysis, and observed

no difference in the rate. He accounted for the phenomenon of autocatalysis in other ways.

The stabilising action of Ba, Cd and Zn salts of 2-ethyl hexanoic acid has been investigated in detail [40,41]. PVC films containing these salts were subjected to various heat treatments. The infra red spectra of these compounds revealed a band at 5.75 which is attributed to the carbonyl stretching frequency of an aliphatic ester. Thus, the stabilising action of these salts was explained on the basis of an exchange of certain chlorine atoms with 2-ethyl hexanoate groups.

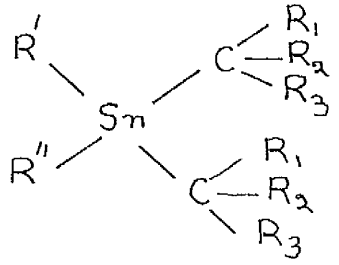


This exchange occurs at the labile chlorine atom. Since the elimination of carboxylic acid from an esterified polymer involves a higher activation energy, than the liberation of HCl, this could account for the stabilisation of PVC by these salts. The occurrence of such interchange reactions have also been confirmed by radioactive tracer work, where PVC film retained radioactivity even after repeated precipitations[41].

It has been suggested that stabilisers act as free radical acceptors[17,39]. Thus Kenyon[39] has proposed the following mechanism for the stabilising action of dibutyl tin diacetate.

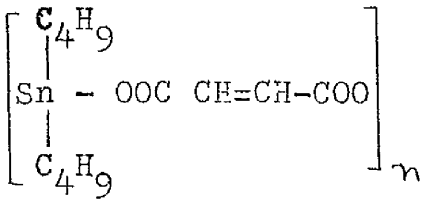
$$R\cdot + (C_4H_9)_2\ Sn(OAc)_2 \longrightarrow RC_4H_9 + C_4H_9\ \dot{S}n(OAc)_2$$

The organo tin stabilisers of the following type have been suggested .

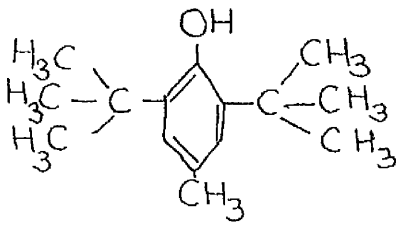



The primary idea which appears to have followed is to facilitate the formation of free radicals by the choice of groups attached to tin atom.

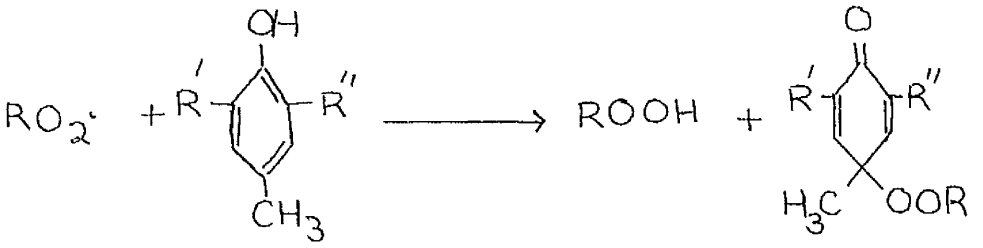
Dibutyl tin maleate was found to be a better stabiliser for PVC than dibutyl tin dilaurate. This suggests the existence of Diels Alders type of addition reaction. Thus the alkaline earth salts of α-β and γ-δ unsaturated acids upto 5 carbon atoms in length have been used (e.g. calcium sorbate, tribasic lead maleate). Dibutyl tin maleate is however preferred.




Antioxidants, of bridged phenolic types are important for preventing discolouration. Mostly phenolic compounds of the following type have been used.



Campbell and Coppinger[42] explains the reaction between $RO_2$ radicals and an alkyl phenol in the following way.



Absorption of light and especially ultraviolet light by the polymer is avoided by adding light screening and opacifying agents such as dibasic lead phosphate, which absorbs in the U.V. region. The selective absorption of light by organic compounds depends on the type and extent of unsaturation. The principal ultraviolet light filters are derivatives of naphthalene, acetyl salicylic acid, and derivatives of benzophenone.

# CHAPTER 2

## Fractionation of PVC

Macromolecular substances exhibit heterogeneity with respect to molecular weight. During polymerisation, polymer chains of varying sizes are produced. The molecular weight distribution can affect the degradation, because a polymer of lower molecular weight might degrade faster than one of high molecular weight. It was, therefore, decided to fractionate the polymer, and thus to obtain fractions having a narrow distribution of molecular weight i.e. more homogeneous in molecular weight than the original polymer.

Several methods of polymer fractionation have been suggested. The Gel filtration method, which is supposed to be a type of molecular sieving in which the solute molecules penetrate the gel particles and are retarded differentially, has been used by Vaughan[44] for the fractionation of polystyrene. The same method when applied to PVC using tetrahydrofuran or cyclohexanone (as solvents) and Santocel A (silica gel) proved unsuccessful. This was due to the tendency of Santocel A to block down the passage of eluting liquid.

The fractional precipitation method involving the addition of a miscible precipitant to a polymer solution was the next choice, because of its reproducibility and high resolving

power[43]. Several solvent and non-solvent pairs are available for PVC fractionation. Cyclohexanone/butanol-1[45] methyl-cyclohexanone/ethanol[46], nibrobenzene/methanol[47], cyclohexanone/heptane[48], cyclohexanone-ethylene glycol[49] and tetrahydrofuran/water[50,51,52] have been employed by various workers for the fractionation of PVC.

In the present work PVC was fractionated using tetrahydrofuran/methanol, cyclohexanone/methanol and tetrahydrofuran/water.

## Experimental

Apparatus for fractionation. The fractionation was carried in a 3 litre, 3 necked flask, having a central B.34 joint and 2 B.19 joints. A mercury seal was attached to the central joint and a glass stirrer was placed here. A flask of similar dimensions, but having a 5 mm. bore stopcock at the bottom as suggested by Hall[53] was rather unsatisfactory, because the fractions which separated out as stiff gels were difficult to remove from it.

Method of fractionation. A known quantity of polymer was placed in the flask and a measured volume of solvent was added so as to give a 1% solution approximately. The solution was left overnight at room temperature to dissolve the polymer. The

flask was then placed in a thermostatic bath adjusted to the desired temperature and the precipitant (methanol or water) was added very slowly through the B.19 joint. The solution was stirred during the addition of precipitant, which was stopped as soon as a turbidity developed. A slow current of nitrogen was passed for 10-15 minutes. The flask was then removed from the bath, and placed in a bath kept at 45°C - 50°C for about 60-90 mins. By this treatment, the low molecular weight polymer which might have been precipitated by the localised increase in concentration of precipitant would dissolve. The flask was then retransferred to the original bath. Nitrogen gas was passed again for some time (30 mins.) and the solution was left overnight to attain equilibrium. The supernatant liquid was then decanted off into another flask. The precipitated phase ($P_1$) which settled at the bottom was removed by dissolving it in acetone and tetrahydrofuran. The decanted liquid was again transferred to the flask. Care was taken to minimise the time of this procedure, because tetrahydrofuran may form peroxides in presence of oxygen. Successive precipitations were carried out in the same way.

The precipitated phase($P_1$) was reprecipitated in an excess of methanol. It was filtered, dried at 45°C and weighed.

In one experiment, the first fraction of lowest molecular weight was collected by total precipitation of the polymer. The polymer solution was poured slowly into an excess of methanol with constant stirring. The solution was left at room temperature to attain equilibrium for 24 hours, and then filtered. The filtrate was reduced in volume by evaporating with a water pump and finally dried on a water bath. This constituted the fraction of lowest molecular weight.

The precipitates were dried at 45°C (± 2°C) and subjected to fractional precipitation as described previously.

The viscosity measurements. The viscosity of PVC solutions was measured in cyclohexanone at 25°C ± 0.1°C in a Ubbelohde viscometer. The concentration of the polymer solution could be altered in the viscometer by adding successive, known volumes of solvents and thoroughly mixing the solution. The flow times between two marks on the viscometer stem were noted for the pure solvent and the polymer solutions. These recordings furnished the relative viscosity of the solution. A polymer concentration of $1.2 \times 10^{-2}$ to $0.3 \times 10^{-3}$ gm. ml.$^{-1}$ was used.

Evaluation of data. The specific viscosity $\eta_{sp}$ of any polymer solution is defined as –

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} \qquad (1)$$

where $\eta$ = viscosity of the polymer solution

$\eta_o$ = viscosity of the pure solvent

From eq. (1) one can write

$$\eta_{sp} = \eta_r - 1 \qquad (2)$$

where $\eta_r$ is called as relative viscosity.

Staudinger proposed a relationship between the specific viscosity of a polymer solution and its molecular weight, but it was soon realised that other factors as rate of shear play an important role in concentrated solutions. This problem could be overcome by extrapolation to infinite dilution. The intrinsic viscosity or limiting viscosity number $\lim_{c \to 0} \eta_{sp}/[C]$ can be obtained from the plot of $\eta_{sp}/[C]$ vs. [C]. Its units normally are 100 ml. gm.$^{-1}$

The limiting viscosity number of fractions obtained by fractionation of PVC in THF/water system, was determined by simultaneous use of two equations in graphical extrapolation - (fig. 1,2).

$$\lambda'' = \lambda''_o (1 - \beta_o C) \text{ equation of Fuoss and Mead}^{54} \qquad (3)$$

where $\lambda''$ = logarithmic viscosity number ($\ln \eta r/C$)

$\lambda''_o$ = limiting viscosity number

C = concentration in monomoles/l

$\beta$ = constant, independent of molecular weight of polymer.

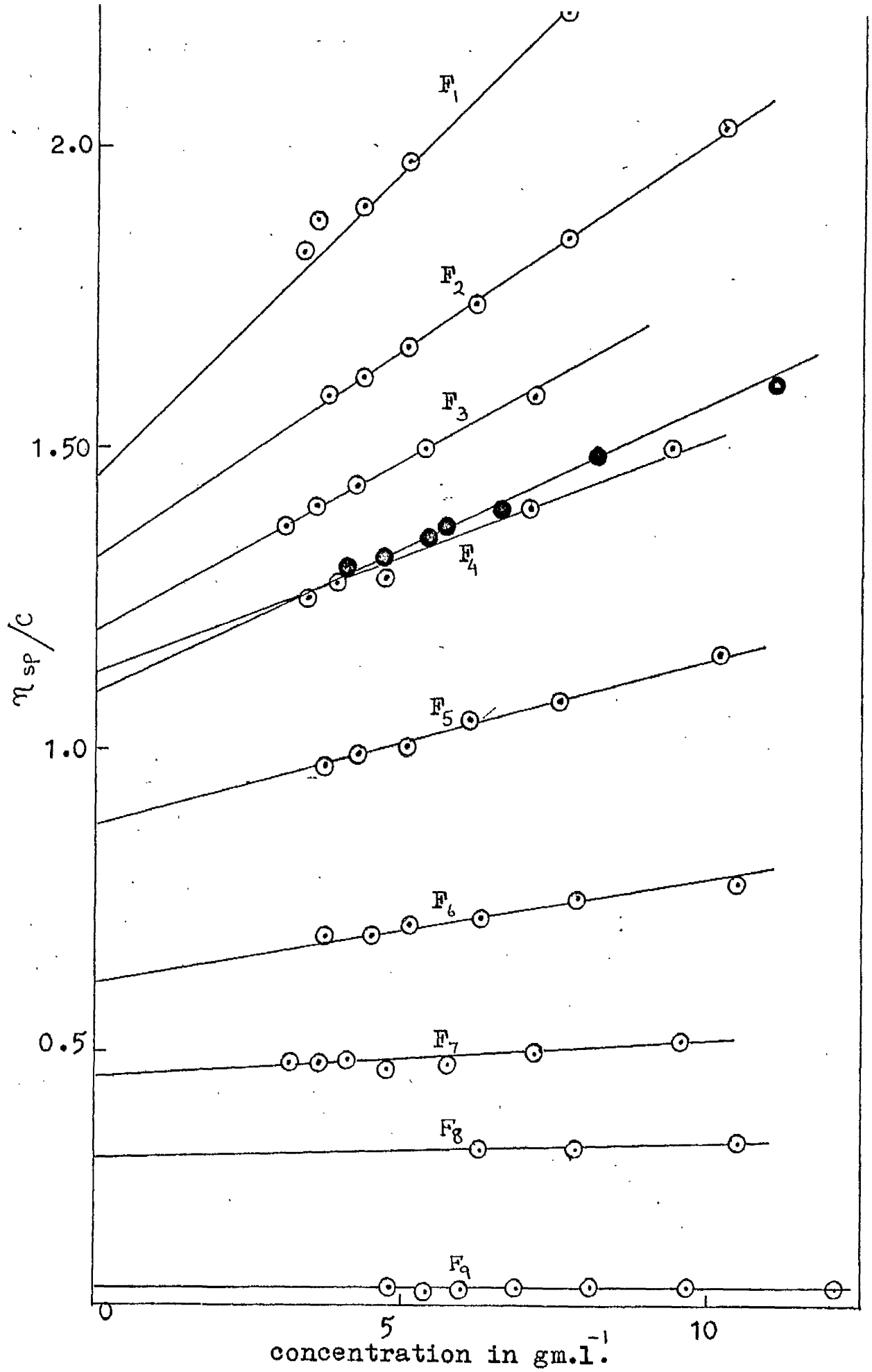



Fig. 1. Intrinsic viscosity determination of PVC fractions in cyclohexanone at 25° C.

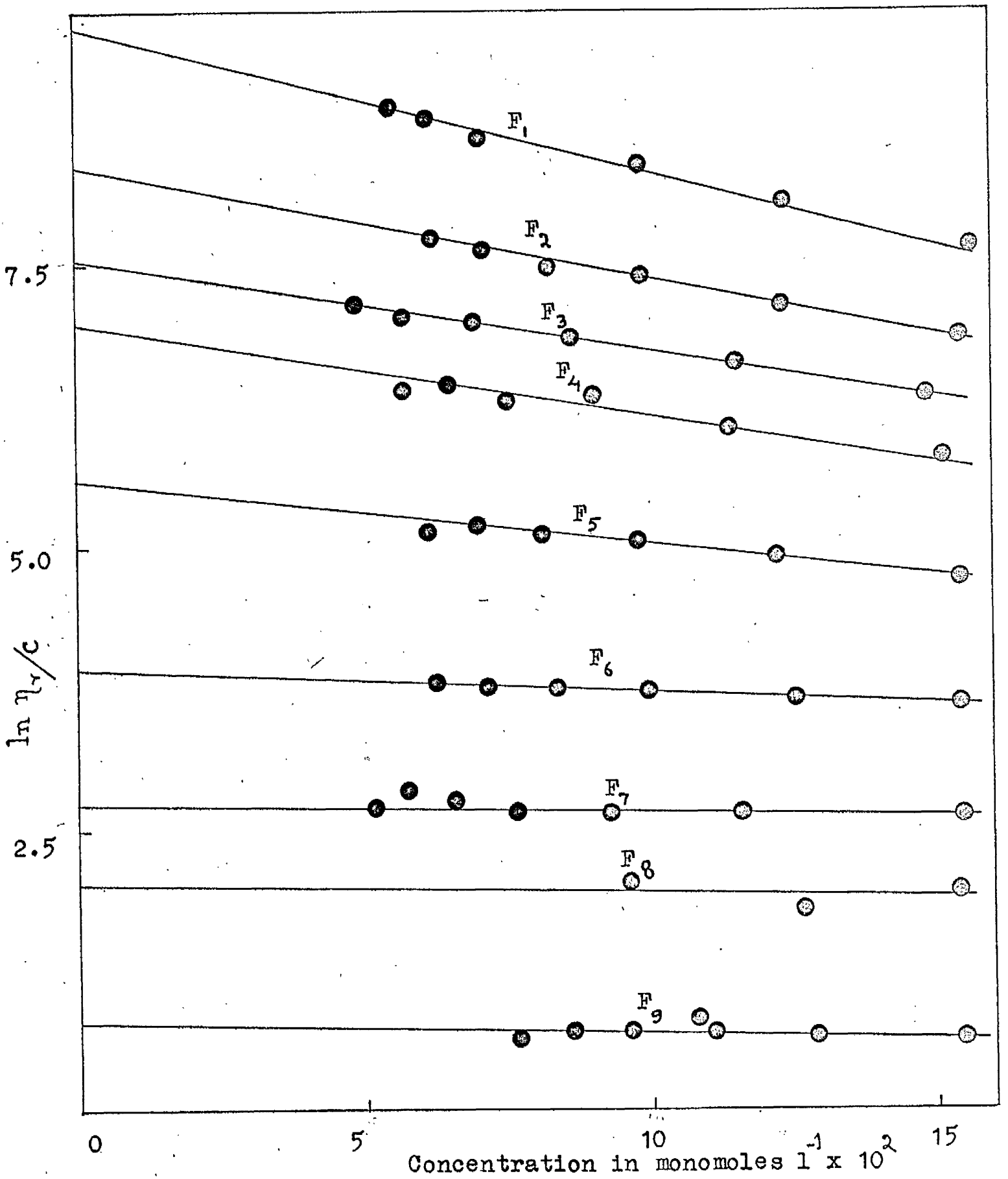



Fig. 2 Determination of limiting viscosity number from logarithmic viscosity for PVC fractions in cyclohexanone at 25°C.

So one viscosity determination would be enough to know the value of $\lambda''_o$ if value of $\beta$ is known.

Second equation employed was of Huggins[55]

$$\eta_{sp}/[C] = \left[\eta_{sp}/[C]\right]_{C=0} + k_1'\left[\eta_{sp}/[C]\right]_{C=0}^{2} C \qquad (4)$$

where C = concentration in $gm.l^{-1}$

$k_1'$ = constant, characteristic of given solute solvent system. It is the same for solutions in a given solvent, of different members of polymer-homologous series.

The value of $\beta$ and $k_1'$ were calculated and are reported in the table.

The purification of solvents -

Cyclohexanone (B.D.H. grade) used for viscometric measurements was purified by distilling under reduced pressure.

Tetrahydrofuran (THF) - Tetrahydrofuran if left in the atmosphere forms peroxides which might act as a catalysts for the degradation of the polymer at high temperatures, and might also induce other undesirable side reactions. THF was, therefore, refluxed over ferrous sulphate ($FeSO_4.7H_2O$) for about 30 minutes to decompose the peroxides. The solution was then decanted off and distilled under nitrogen at 63°C - 64°C. The distillate could be used for 5 or 6 days if kept under nitrogen in brown bottles. Acetone,

methanol etc. were used as supplied without any further purification.

## Results

The results of fractionation of polyvinylchloride using cyclohexanone or tetrahydrofuran as solvents and methanol as precipitant are given in table 1 and 2.

### Table 1

Fractionation of JLB-49 using cyclohexanone and methanol

Wt. of polymer = 10.1008 gm. = 1.15 dl gm.$^{-1}$

Temperature of precipitation = 27.4°C

| No. | Volume of precipitant mls. | wt. of fractions (gms.) | Intrinsic viscoisty dl gm.$^{-1}$ |
|---|---|---|---|
| 1 | 650 | 4.0000 | 1.34 |
| 2 | 35 | 2.6132 | 1.31 |
| 3 | 50 | 0.1622 | 1.04 |
| 4 | 50 | 0.2252 | 0.77 |
| 5 | 40.0 | 0.1098 | - |
| 6 | 63.0 | 0.2292 | - |
| 7 | 100.0 | 0.2712 | - |
| 8 | 150.0 | 0.2430 | - |
| 9 | 175.0 | 0.0910 | - |
| 10 | 700 | 0.1620 | 0.45 |

Table 2

Fractionation of JLB-49 using THF and methanol

Wt. of polymer = 9.9450 gm., = 1.15 dl. $gm.^{-1}$

Temperature of precipitation 27.4°C

| No. | Volume of precipitant in mls. | Wt. of fractions gms. | Intrinsic viscosity $dl.gm.^{-1}$ |
|---|---|---|---|
| $a_1$ | 950 | 0.9994 | 1.23 |
| $a_2$ | 47 | 5.1880 | 1.40 |
| $a_3$ | 55 | 1.5936 | 0.78 |
| $a_4$ | 80 | 0.3146 | 0.47 |
| $a_5$ | 75 | 0.3190 | - |
| $a_6$ | 50 | 0.0884 | - |
| $a_7$ | 105 | 0.1322 | - |
| $a_8$ | 200 | 0.2060 | - |
| $a_9$ | 250 | 0.0236 | - |
| $a_{10}$ | 850 | 0.2274 | 0.115 |

The intrinsic viscosity of second fraction of THF-methanol system is higher than the first fraction. More than half of the polymer is precipitated out. It was decided to fractionate this second fraction again.

Table 3

Fractionation of second fraction (table 2) using

THF-methanol system

Wt. of polymer = 4.8374 gm., $[\eta]$ = 1.40 dl. gm.$^{-1}$

Temperature of precipitation = 27.4°C

| No. | Volume of precipitant in mls. | Wt. of fractions gms. | Intrinsic viscosity dl.gm.$^{-1}$ |
|---|---|---|---|
| $S_1$ | 440 | 0.6626 | 1.21 |
| $S_2$ | 15.0 | 0.2429 | 1.34 |
| $S_3$ | 20.0 | 1.4688 | 1.36 |
| $S_4$ | 26.0 | 1.2576 | 1.48 |
| $S_5$ | 15.0 | 0.3170 | 1.34 |
| $S_6$ | 30.0 | 0.1420 | - |
| $S_7$ | 50 | 0.1316 | - |
| $S_8$ | 150 | - | - |

## Table No. 4

### Fractionation of JLB-49 using THF and water

Wt. of polymer = 12.3170 gm., $[\eta]$ = 1.10 dl. gm.$^{-1}$

Temperature of fractionation = 25°C

| No. | Wt. of fractions gms. | $W_x$ | $[\eta]$ dl. gm.$^{-1}$ | $\lambda''_o$ | $k'_1$ | $\beta$ |
|---|---|---|---|---|---|---|
| $F_1$ | 4.5318 | 0.8164 | 1.45 | 9.6 | 0.4694 | 0.1390 |
| $F_2$ | 1.9904 | 0.5481 | 1.32 | 8.35 | 0.4646 | 0.1388 |
| $F_3$ | 0.2472 | 0.4546 | 1.20 | 7.55 | 0.3858 | 0.1433 |
| $F_4$ | 1.4842 | 0.3819 | 1.25 | 6.95 | 0.3061 | 0.1606 |
| $F_5$ | 1.3558 | 0.2651 | 0.875 | 5.60 | 0.311 | 0.1839 |
| $F_6$ | 1.3188 | 0.1551 | 0.615 | 3.95 | 0.4564 | 0.1436 |
| $F_7$ | 0.6176 | 0.0765 | 0.460 | 2.75 | 0.2554 | 0.1225 |
| $F_8$ | 0.3030 | 0.0376 | 0.320 | 2.05 | 0.2919 | 0.2163 |
| $F_9$ | 0.3066 | 0.0126 | 0.110 | 0.80 | 0.00 | 0.1953 |

The $\Sigma w_i[\eta_i]$ (where $w_i$ = weight of ith fraction and $[\eta_i]$ = intrinsic viscosity) value for all the fractions gave a value of 13.5858 which is in very good agreement with the value of 13.5487 obtained by multiplying the weight of polymer (12.3170 gm.) with the intrinsic viscosity (1.10 dl. $g.^{-1}$)

The integral weight distribution curve is obtained by plotting the cumulative weight less half the weight of the last fraction against $[\eta]$. Thus, the integral weight distribution function is obtained by taking the weight of the fraction per gram of polymer of lowest intrinsic viscosity and adding it to half the weight of the fraction of higher intrinsic viscosity. The subsequent additions in this manner gave the value of $w_x$ for each fraction. A plot of $W_x$ vs. the corresponding value of $[\eta]$ gave the integral weight distribution curve (fig. 3).

The differential weight distribution curve (fig. 4) was obtained by the graphical differentiation of the integral curve.

A large scale fractionation of PVC starting with 20 gms. of polymer was also performed. Only first three fractions were collected. The weight and intrinsic viscosity of the fractions were $b_1$ = 7.86 gm. $[\eta]$ = 1.48 dl. $gm.^{-1}$ $b_2$ = 5.07 gm. $[\eta]$ = 0.94 and $b_3$ = 1.262 gm.

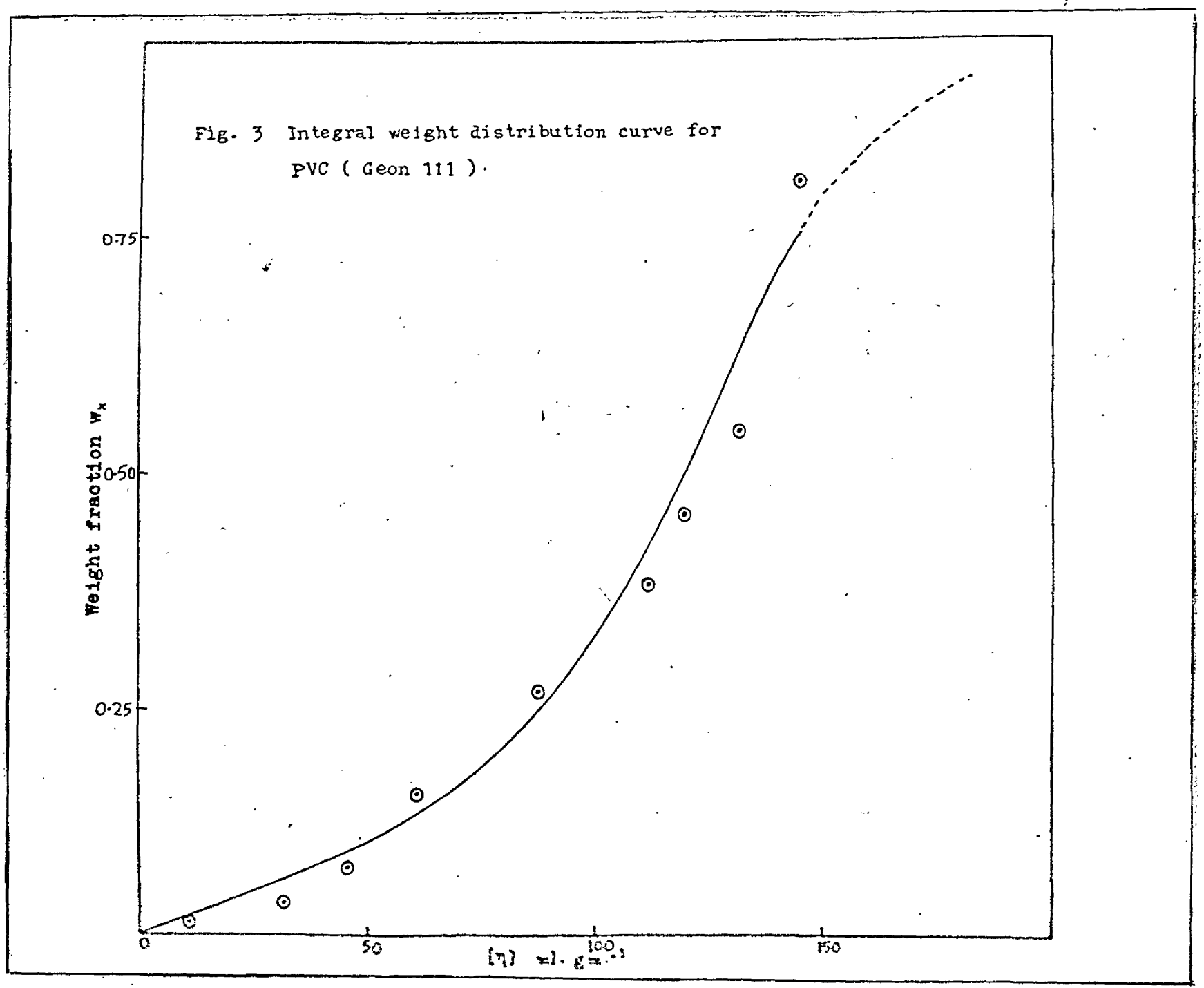


Fig. 3 Integral weight distribution curve for PVC ( Geon 111 ).
0·75
0·50
0·25
Weight fraction $w_x$
0
50
100
150
[η] ml. g⁻¹

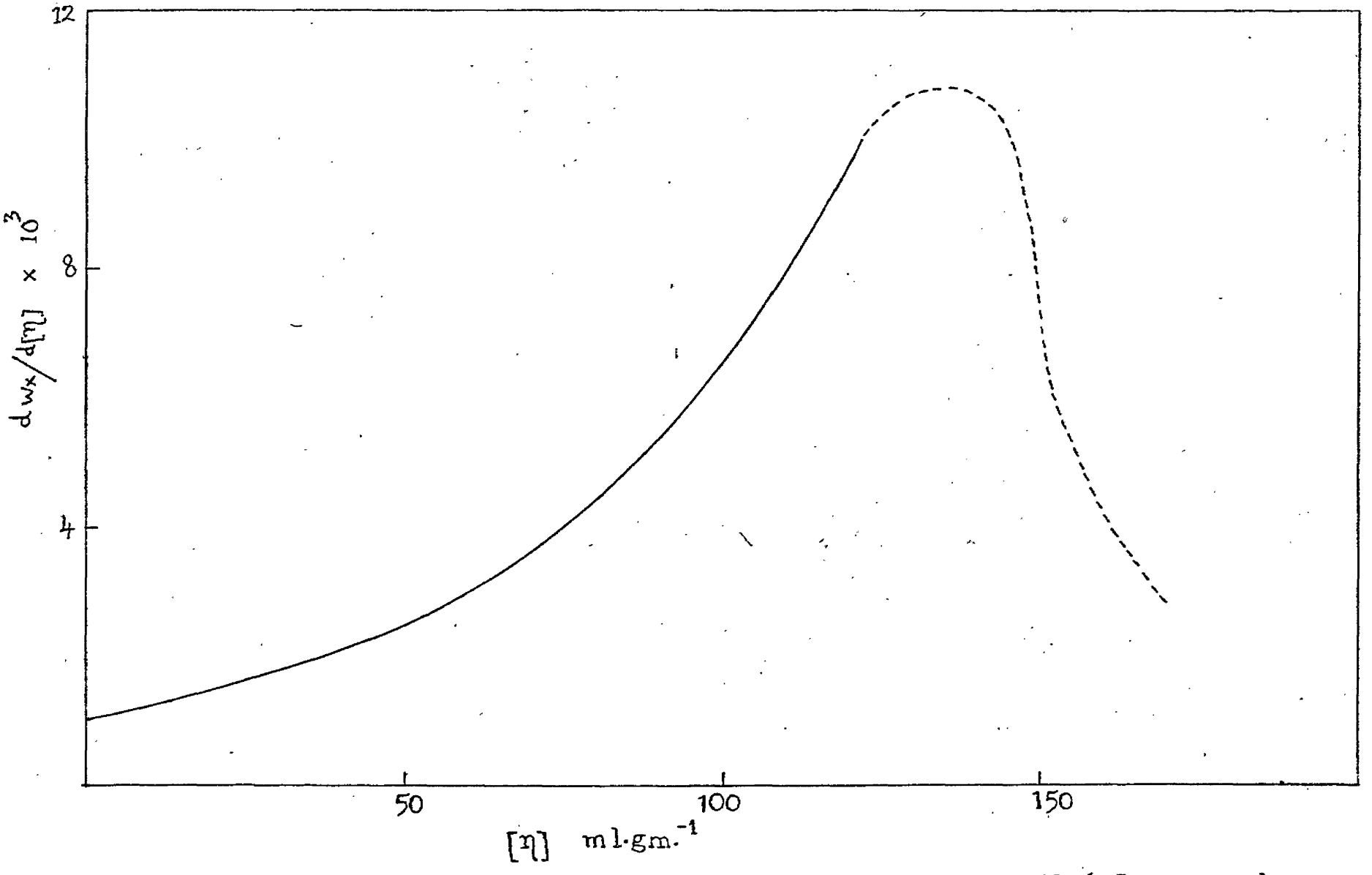



Fig. 4 Differential weight distribution curve for PVC ( Geon 111 ).

## Discussion

Table 2 and 3 indicate clearly that a reverse precipitation of polymer in system THF and methanol has taken place.

Association of PVC in poor solvent media has been reported. Mencik[56] has observed that in systems like cyclohexanone and tetrahydrofuran as solvents and aliphatic monohydric alcohols as precipitants, the fractionation does not proceed on molecular weight basis. He has based this argument on the turbidimetric titrations. A plot of $[\eta]$ vs. $\gamma'$ (volume fraction of precipitant added that produces the first haze) gave a linear relationship for systems like THF and water or cyclohexanone-ethylene glycol. There is a deviation from linear relationship for THF amyl alcohol (and other alcohol systems) which make the precise fractionation on a molecular weight basis difficult with these systems.

A plot of $[\eta]$ vs $\gamma'$, obtained from the data of table 2 is shown in fig. 5, and for comparison the plot obtained by Mencik[56] is also given. Whereas Mencik obtained first four fractions of similar intrinsic viscosity we got a second fraction of higher intrinsic viscosity than the first. A sub-fractionation of this second fraction yielded fractions which again showed reverse precipitation. The intrinsic viscosity of the first four fractions increased very gradually (table 3). It is very difficult to explain this phenomenon solely by association, because in that

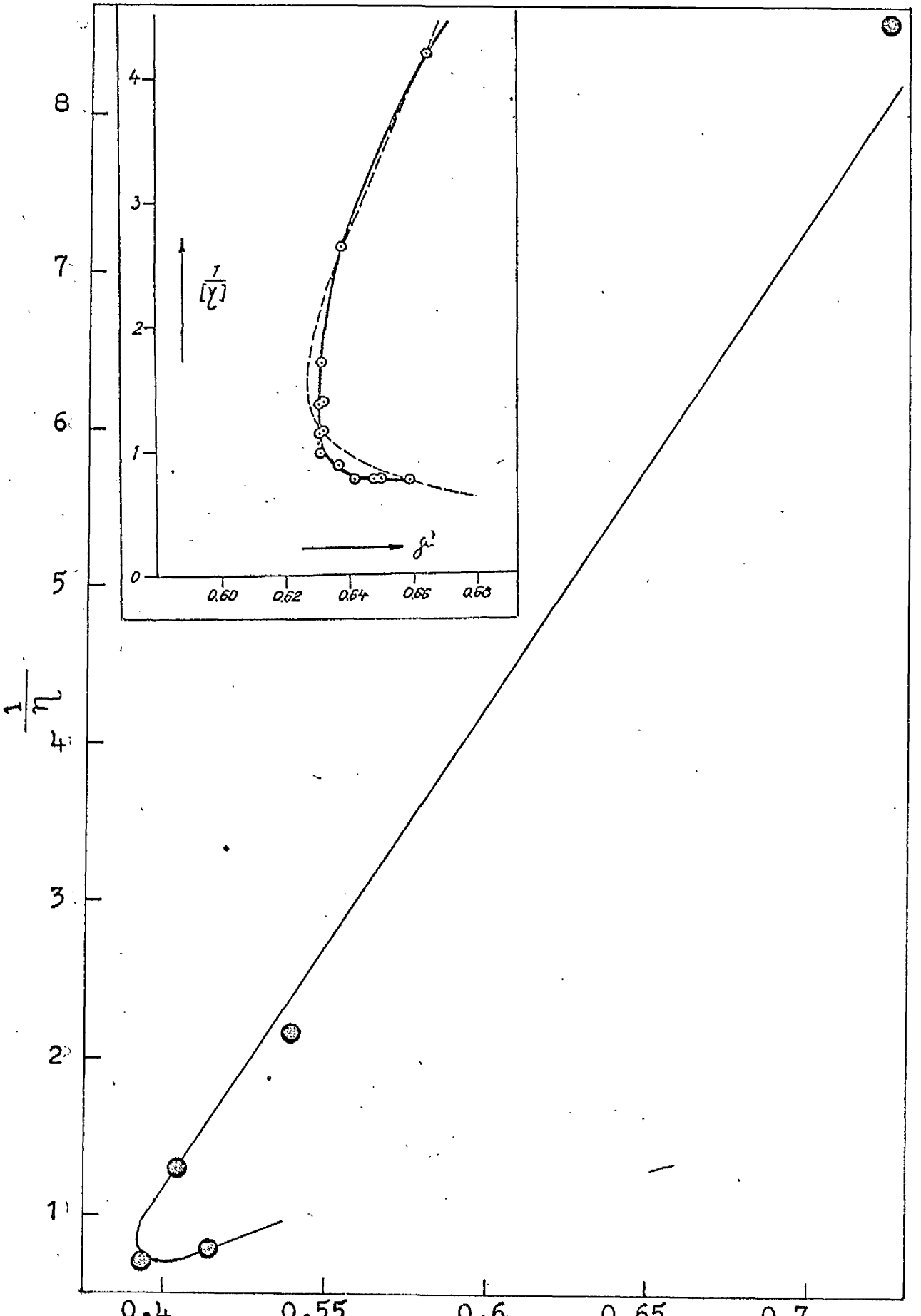



Fig. 5 Dependence of the precipitation point on the fraction of PVC in the system THF-MeOH.

case one would have expected to obtain fractions of decreasing intrinsic viscosity, by the subfractionation.

Another possibility is the selective separation of crystalline polymer. A fraction of lower intrinsic viscosity but of greater crystallinity might precipitate before a fraction of higher intrinsic viscosity and lower crystallinity. Kobayashi[52] observed that the $[\eta]$ of the fractions of low temperature polymerised PVC increased with increase in fraction number, came to a maximum value and then decreased in the usual manner. This clearly indicates that fractionation depends not only on the molecular weight of the polymer, but also on the chain regularity. The absorbance ratio of bands at 635 and 690 $cm.^{-1}$ of i.r. bands in the solid film have been used as a measure of stereoregularity of PVC[57,58]. The band at 690 $cm.^{-1}$ is assigned to C-Cl stretching vibration of folded chain conformation (i.e. mainly isotactic configuration) and the band at 635 $cm.^{-1}$ is assigned to C-Cl stretching vibration of extended chain conformation (mainly syndiotactic configuration)[59]. This method of assessing the crystallinity of PVC has been used by several workers[60-63]. The same method was used here. A Perkin-Elmer model 125 spectrophotometer was used and the scanning was done in the region 550 $cm.^{-1}$ - 750 $cm.^{-1}$. The PVC films were prepared from a 3% THF solution, by evaporating it on a plain glass surface at 45°C (approximately). A typical spectra is shown in fig. 6. The results of these investigations are tabulated in table 5 .

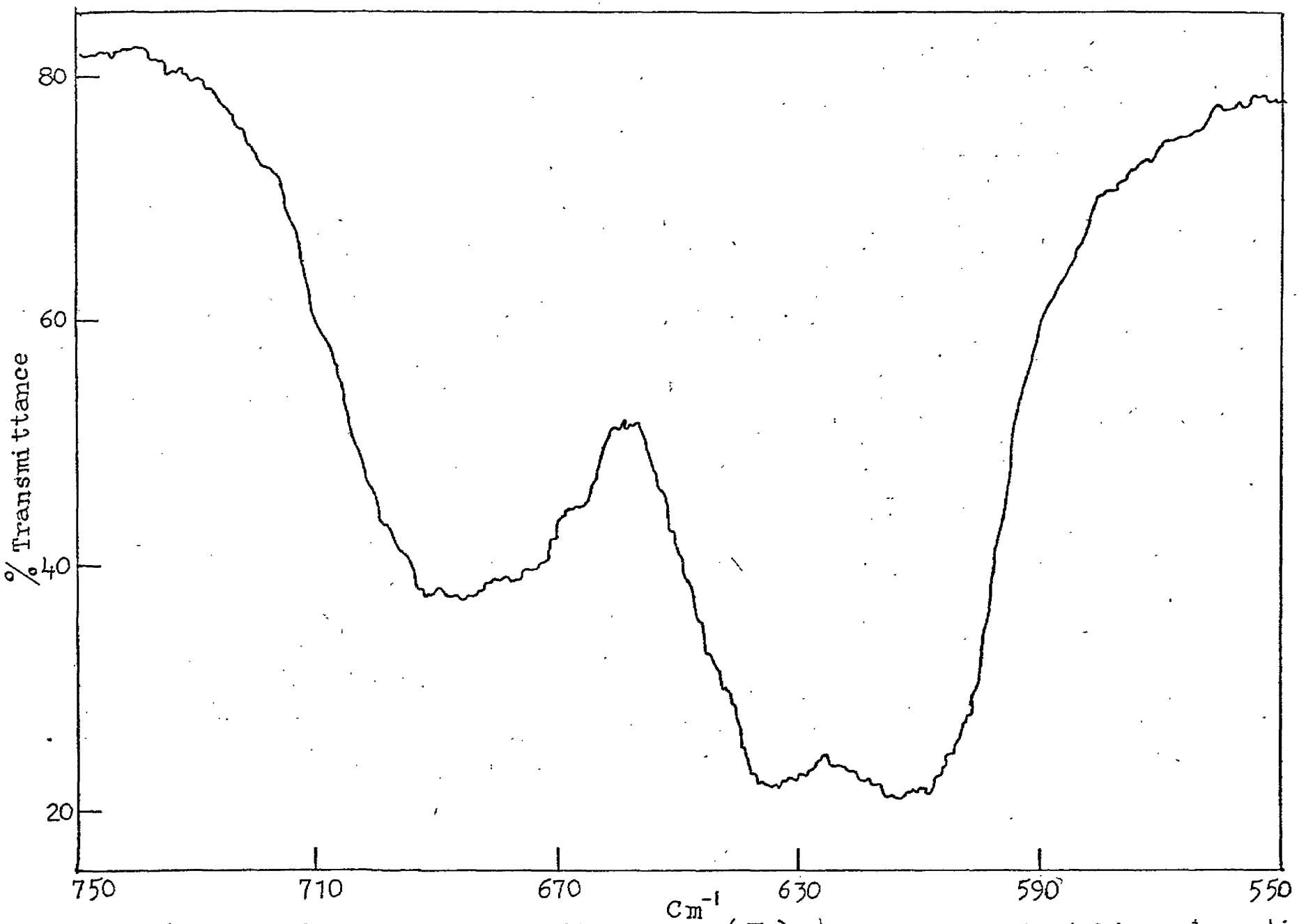



Fig. 6 Far infra red spectra of PVC film ($F_2$) showing C-Cl stretching absorption bands due to syndiotactic and isotactic units.

Table 5

The i.r. absorption spectra results, showing crystalline syndiotactic units in the polymer.

| Fraction No. | Intrinsic viscosity | Absorbance ratio 635/690 $cm.^{-1}$ |
|---|---|---|
| Whole polymer | 1.10 | 1.46 |
| $a_1$ | 1.23 | 1.41 |
| $s_1$ | 1.21 | 1.51 |
| $s_3$ | 1.3 | 1.35 |
| $s_4$ | 1.48 | 1.24 |
| $F_2$ | 1.32 | 1.32 |
| $F_7$ | 0.46 | 1.56 |

It is quite clear from this table that the crystallinity of fractions $s_1$, $s_3$ and $s_4$ decreases though the intrinsic viscosity has increased. The separation is evidently on the basis of crystallinity and not on intrinsic viscosity in this case. However, the crystallinity of $F_7$ is more than $F_2$ but the fractionation in this case does not occur on basis of crystallinity. Perhaps in the systems like THF and methanol, the lower molecular weight crystalline material is adsorbed on the higher molecular weight polymer, and this crystallinity than becomes the determining factor of fractionation. Lower molecular weight materials are

generally more crystalline than high molecular weight polymer. Thus aldehydes have been used as polymerisation media to obtain crystalline PVC[62].

The intrinsic viscosity of the fractions obtained from the cyclohexanone-methanol system lies between 0.45 dl. gm.$^{-1}$ to 1.34 dl.gm.$^{-1}$ Though no reverse precipitation was observed (contrary to the finding of Moncik) yet the resolving power of the system is not very high.

The fractionation of PVC using THF and water gave fractions, the intrinsic viscosity of which varied between 0.10 dl./g. to 1.45 dl./g. About 65% of the polymer separates out between 1.10 dl./g. - 1.45 dl./g. Thus in suspension polymerisation, most of the high molecular weight polymer is produced.

The k' values (in Huggin's equation) vary between 0.49 to 0.29 with the exception of ninth fraction where the values are zero. These values are similar to those found by Pezzin[8] (0.3 - 0.4) for PVC. The mean average value for k' + $\beta$ is equal to 0.49 which is similar to the value of 0.504 obtained by Pezzin et. al.[8]

The fractions obtained from THF/$H_2O$ system have been used for the degradation studies using ultraviolet spectrophotometry. The molecular weight of few of these fractions was determined using light scattering technique.

# CHAPTER 3

## The thermal degradation of polyvinylchloride in solution

The thermal degradation of polyvinylchloride in solid state (powder or film) has beenextensively investigated[10,11,16,21,22]. However, there is a possibility of diffusion control of the evolved gases in solid state degradation. Solution degradation, facilitates the diffusion of evolved gases, and also enables to determine the dependence of the rate on the polymer concentration.

Bengough and Sharpe[9] have investigated the degradation of PVC in solutions using ethylbenzoate, O-dichlorobenzene and nitrobenzene as solvents. The work was further extended by us, and benzyl alcohol, tritoluylphosphate, dioctylphthalate, benzophenone, and dichloronaphthalene were used as solvents for studying the polymer breakdown in the temperature range of 187°C - 243°C.

### Experimental

#### Apparatus used for pyrolysis

The pyrolysis unit as devised by Bengough and Sharpe[9] was used to carry out the degradation. The various parts of the unit are shown in fig. 7, and can be divided into three parts. (1) The vapour jacket or heater consists of a cylindrical body with a side arm to receive a water condenser. It also contains a thermometer socket. It has a B-24 cone at one end

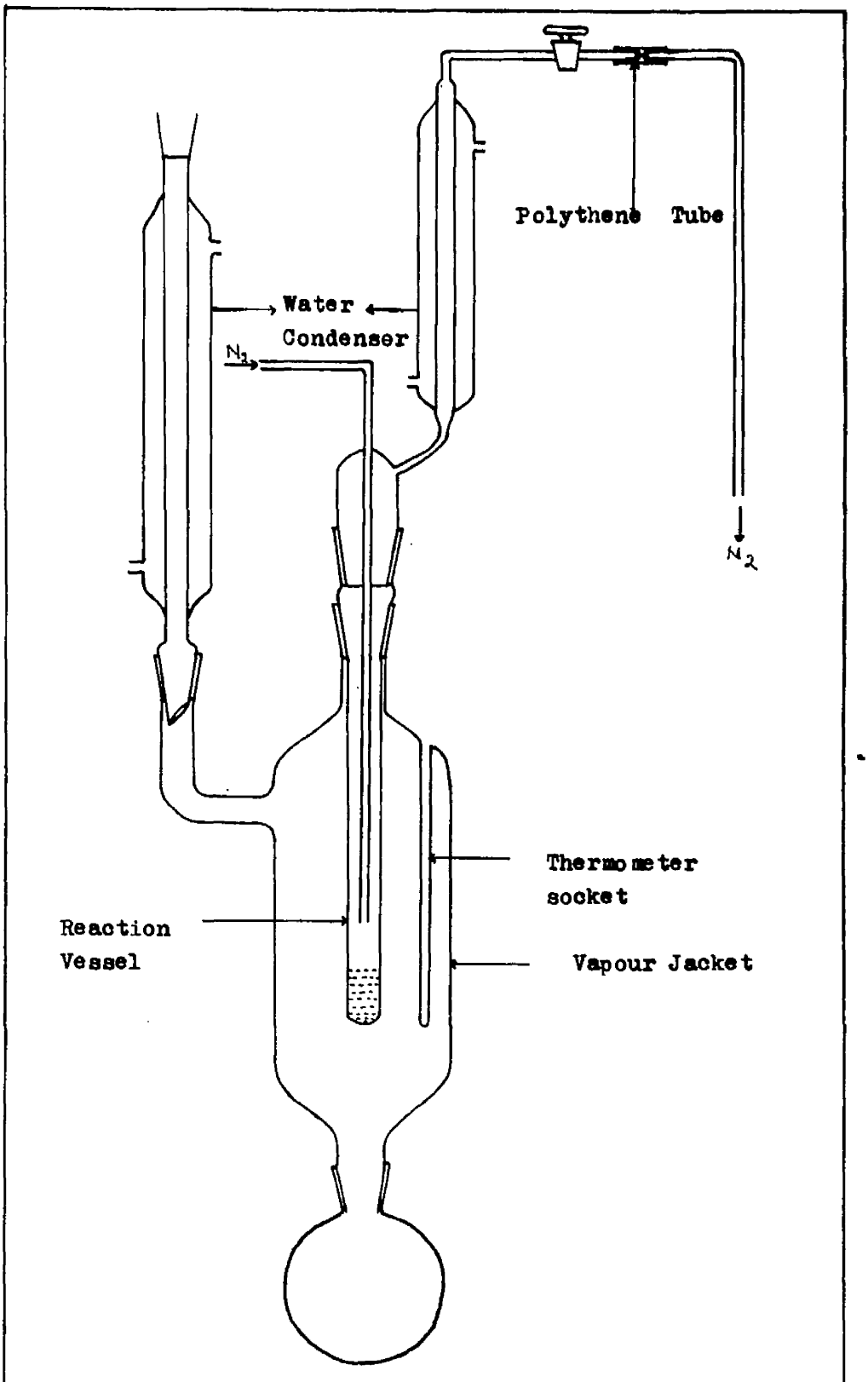



Fig. 7. Degradation Apparatus ( Heating Unit ).

and a B-24 socket at the other end. The B-24 cone of the vapour jacket fits into a B-24 socket of a 250 ml. round bottom flask. This flask contains the heating medium (solvent) and is heated by an electrothermal heating mantle. An asbestos coil or sheet is placed around the vapour jacket to prevent heat loss.

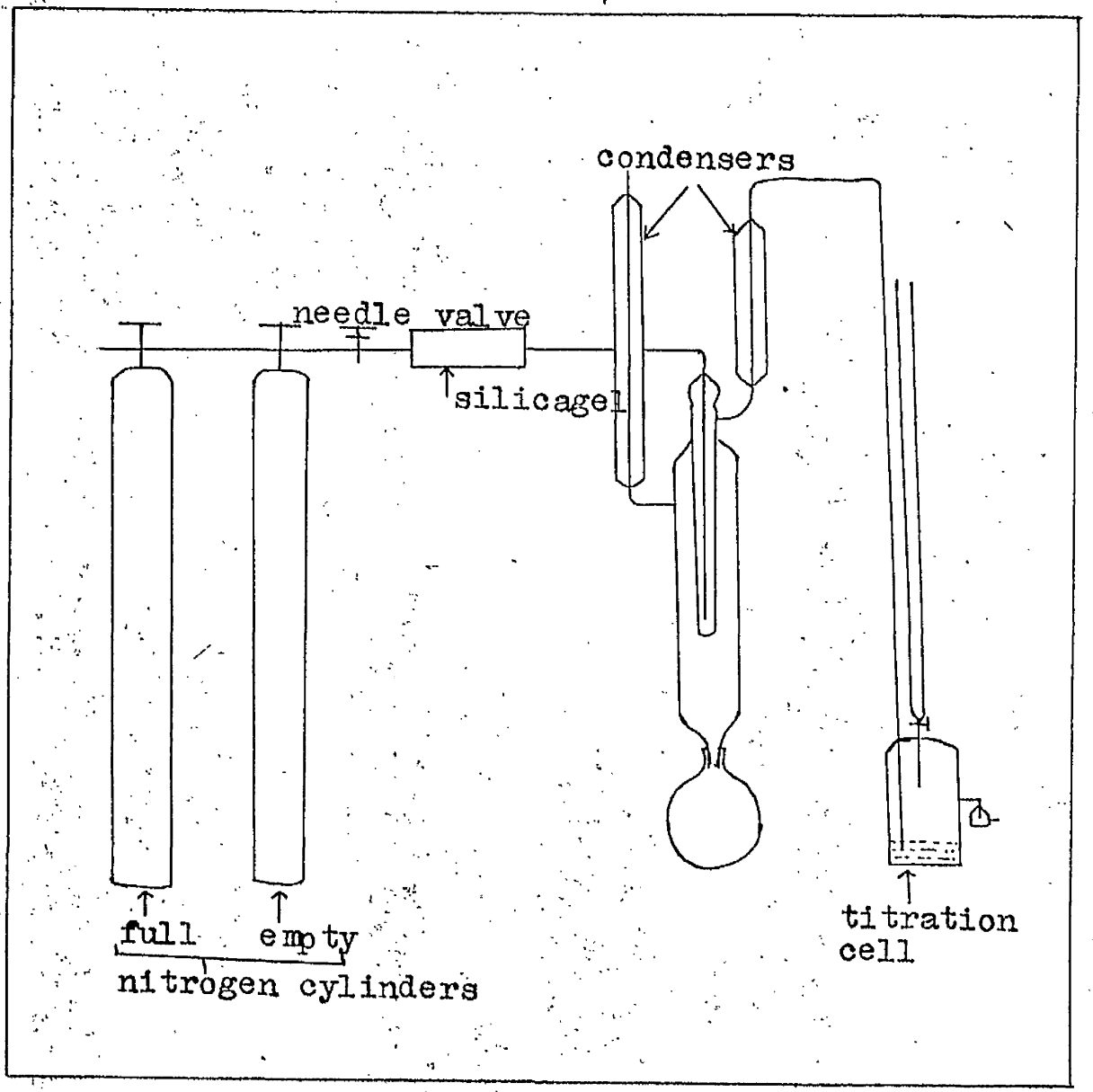
(2) The reactor is a Pyrex glass tube having a B-24 cone joined to the B-24 socket at the upper part. The B-24 cone fits into the socket of vapour jacket. The length of the tube from the B-24 cone to the bottom end is 16 cms.

(3) The still head comprises of a Drechsel head which fits into the B-24 socket of the reactor. The Drechsel head is attached to a water condenser.

The flow system. White spot nitrogen gas was used for sweeping out the gases produced during the thermal degradation of the polymer. The flow of nitrogen was controlled by connecting a full nitrogen cylinder to an empty one which was used as a low pressure reservoir. Further flow of nitrogen is controlled by means of a needle valve. The whole set up is shown in fig. 8.

The recording system. The progress of the reaction was followed volumetrically. Acid evolved during pyrolysis was swept into a glass cell containing distilled water and indicator (bromothymol blue) and was titrated against N/100 sodium hydroxide at regular intervals of time. Bromothymol blue changes colour even

Fig. 8 Set up of degradation unit



when it is stirred in air i.e. the carbon-dioxide present in air is sufficient to cause a colour change (pH 6-7.6). It was, therefore, necessary to prevent the contents of the glass cell from coming into contact with air. This was achieved by using the arrangement shown in fig. 9. The inlet for the burette was normally closed with a stopper and opened only at the time of titrations.

Heating media. The solvents selected for maintaining different temperatures were - p-cymene (178°C) decalin (187°C) ethylene glycol (198°C) ethylbenzoate 212.6°C, m-nitrotoluene (231°C) and diethylene glycol (243°C).

Solvents for polymer. As has already been mentioned PVC degr ded in solution in the temperature range of 187°C - 243°C. The boiling points of the selected solvents should, therefore, be above 250°C. Furthermore, they should not react with the polymer at higher temperatures. The following four solvents fulfilled these conditions, (1) benzophenone (B.D.H.) (2) dioctylphthalate (British Geon Ltd.) (3) tritoluylphosphate (British Geon Ltd.) and (4) dichloronaphthalene (Eastman Kodak Co.).

A few runs were also done using ethylbenzoate (B.D.H.) b.p. 212.6°C and benzyl alcohol (b.p. 205°C) as solvents. Due to the low boiling points of these solvents, the degradations were studied at 178°C, 187°C and 198°C in benzyl alcohol and

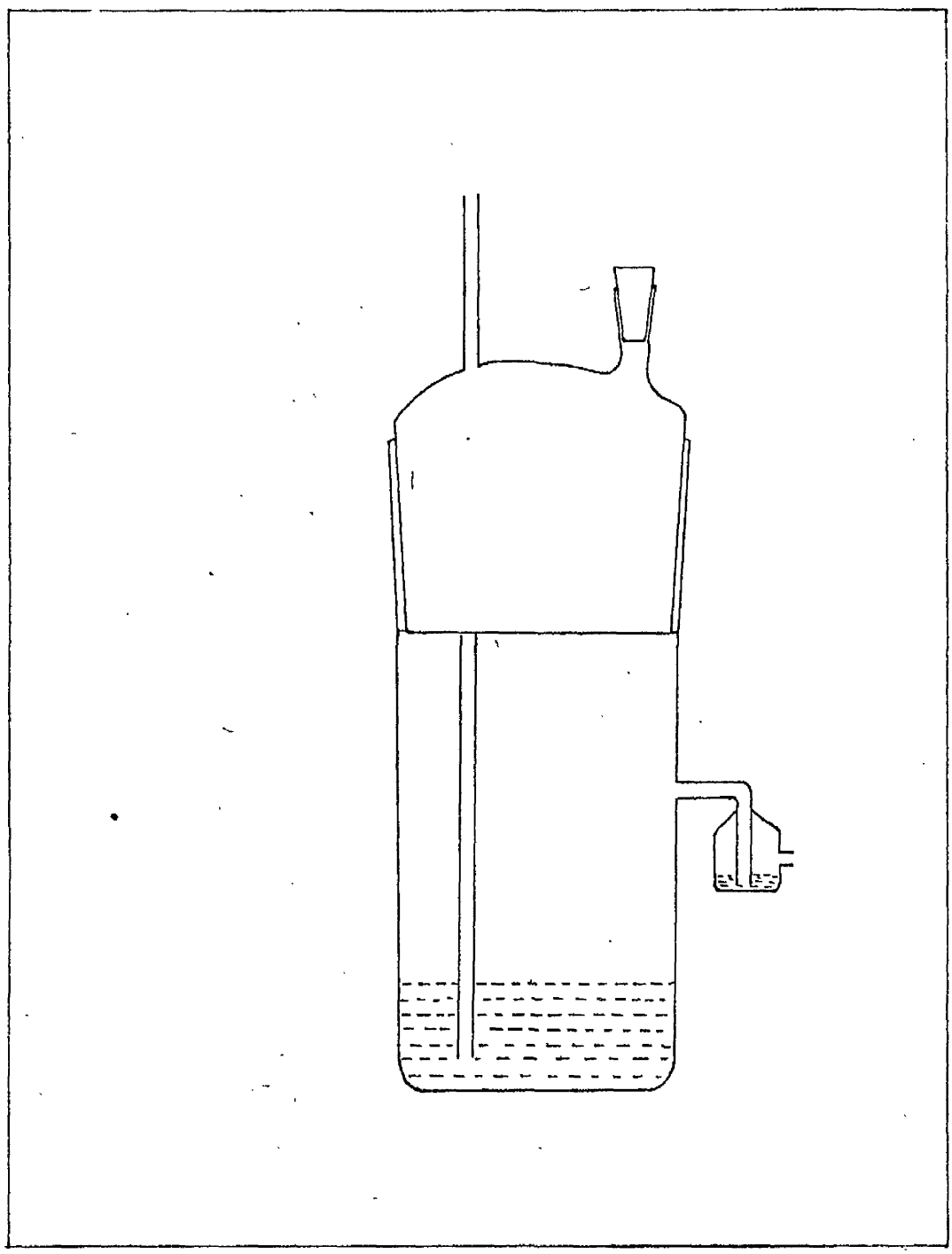


Fig. 9 Titration Cell

at 187°C, 198°C and 212.6°C in ethylbenzoate.

All of the above mentioned solvents were used without any purification except dichloronaphthalene which was purified by crystallising it from methylalcohol at 0°C.

Analytical Reagents. Sodium hydroxide as supplied by B.D.H. in concentratedvolumetric solutions in polythene ampoules was used after proper dilutions.

Description of a typical run. At the start of pyrolysis the heater was switched on. The apparatus was left for some time until thermal equilibrium was attained. A weighed quantity of polymer was placed in the reactor tube and dissolved in 2 ml. of solvent by warming. The reactor tube was then transferred to the vapour jacket and the Drechsel head was placed in the B-24 socket of the reactor. The flow of nitrogen was started, and the nitrogen emerging from the reaction vessel was bubbled through distilled water. The time was noted by a stop watch.

When it was desired to change the heating media to attain different temperatures, the vapour jacket and flask were thoroughly washed with benzene followed by acetone and water. Finally, these were dried and the new liquid was introduced into the flask.

Cleaning of the reactor. It was convenient to clean the reactor immediately after use. The contents were poured out, and the reactor was washed with acetone followed by water. It was then

left overnight in either concentrated nitric acid or chromic acid - $H_2SO_4$ bath. Subsequent washing with water and acetone removed all the polymer sticking to the sides of the walls.

Polymer. The commercial polymer JLB-49 (Geon 111) as supplied by Distiller's Company Ltd., is contaminated with impurities such as the catalysts used in polymerisation, suspender agents and traces of metal salts. The existence of traces of catalyst in the polymer was indicated by a fast initial rate of dehydrochlorination in nitrogen which dropped with time. These experiments on the dehydrochlorination of commercial polymer were not reproducible. This might be explained by an uneven distribution of catalyst in the polymer particles. It was, therefore, decided to purify the polymer.

Two methods of purification were used -

(1) to wash the polymer with acetone

(2) to totally precipitate a tetrahydrofuran (THF) solution of polymer with methanol.

Both of the methods will be discussed separately

(1) Washing with acetone. About 10 gms. of polymer were kept in 4 conical flasks (roughly 2.5 gms. in each flask) and 50 ml. of acetone was added to each flask. The flasks were shaken for one hour by means of a mechanical shaker. The acetone was decanted off, and collected in a separate flask. A further, 50 ml. of the acetone was added to the flasks and stirred again.

This process was repeated five times, and altogether six acetone washings were collected. The polymer was dried at 50°C and weighed.

The acetone washings, were concentrated and finally dried in vacuo at room temperature. The dried residue, slightly yellow in colour was weighed. It was observed that about 9.4% of the total polymer weight was removed by acetone extraction.

An attempt was made to identify the components of this acetone soluble residue.

A thin film of this residue was suspended in methanol for six days. This was done to dissolve the catalyst or stabiliser while leaving the low molecular weight PVC insoluble. However, the infra red spectra of film before and after suspending it in methanol showed no difference. Subsequent suspension of film in carbon tetrachloride or dilute nitric acid was also without effect.

The infra red spectra of a film (cast from THF solution) of this acetone soluble part showed the presence of several peaks different from those observed in the acetone insoluble portion (fig. 10). Four small peaks were observed in the region 3448 $cm.^{-1}$ to 4348 $cm.^{-1}$ The OH stretching frequencies usually lie in this region. The corresponding OH deformation (1050 $cm.^{-1}$) and CO stretching frequencies (1260 $cm.^{-1}$) could not be identified due to the presence of polymer peaks in this region. There is,

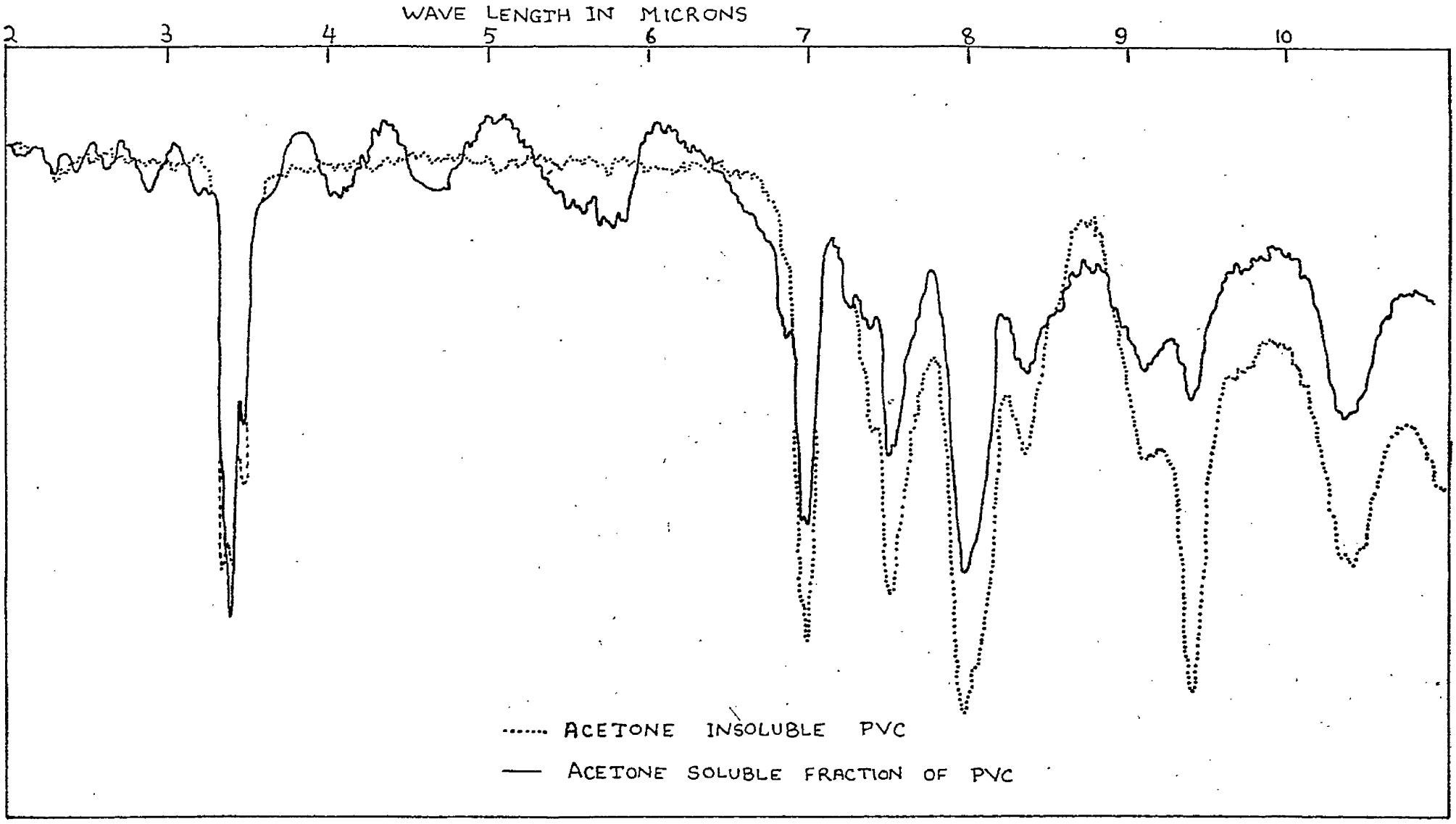


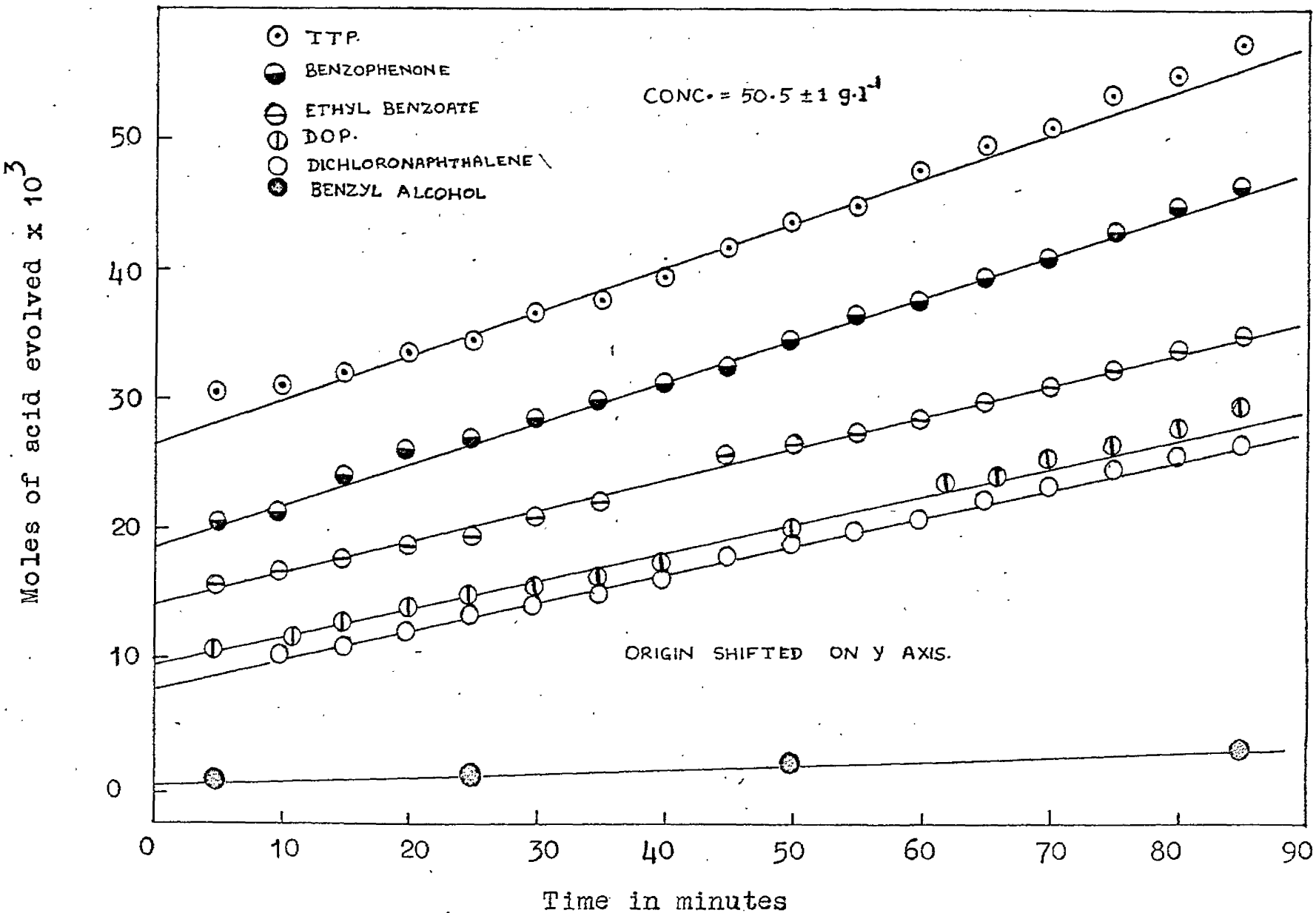

Fig. 10. Infra Red spectra of PVC (GEON 111) film.

also, the appearance of three broad bands in the region 2450 $cm.^{-1}$ - 1695 $cm.^{-1}$ with a small shoulder at 2770 $cm.^{-1}$ Conjugated double bonds, C=O groups etc. appear in this region. Thus the presence of these bands in this region perhaps indicate the presence of catalyst (as benzoyl peroxide) or unsaturated groups. However, due to the complexity of this residue, it is very difficult to conclude anything from i.r. alone. A u.v. spectra of this sample in tetrahydrofuran gave some small peaks at 300, 320 and 350 m $\mu$. Absorption at 350 m $\mu$ may be due to the presence of five conjugated double bonds.

The presence of iron was indicated when the sample was tested with ammonium thiocyanate. The intrinsic viscosity of this fraction in cyclohexanone at 25°C was 0.308 $dl.\ gm.^{-1}$ Degradation of this sample, as followed by u.v. spectrophotometry in dioctylphthalate, revealed that long chained polyene structures are not produced. The rate at which the absorption peak at 350 m $\mu$ increases is much faster than with the acetone insoluble part.

Total precipitation. A weighed sample of polymer was dissolved in THF and diluted with acetone. It was then gradually poured into excess of methanol with constant stirring. The precipitated polymer was allowed to settle at room temperature for 24 hours and then filtered. The filtrate was concentrated, dried and weighed. About 2.5% of the total weight of polymer was removed

Fig.11. Dehydrochlorination of PVC in different solvents at 198°C



by total precipitation. The intrinsic viscosity of the soluble part in cyclohexanone at 25°C was 0.11 dl. gm.$^{-1}$.

Thus the loss in weight is less in the total precipitation process than in the acetone extraction process. Also the intrinsic viscosity of the soluble part is lower. This indicated that loss of the lower molecular weight polymer is removed by precipitation. The rate of dehydrochlorination of both the acetone insoluble part and the precipitated polymer was similar. It was therefore decided to use total precipitation as a means of the purification of the polymer as less polymer is lost by this method.

## Results

### Effect of solvents on the thermal degradation of PVC

The rates of dehydrochlorination of PVC at 198°C in different solvents are shown in fig. 11. It is evident, there is no acceleration in rate with time. A continuous increase in the rate would have been expected if the solvents were attacking the polymer, (as in nitrobenzene[9]). The rate of dehydrochlorination varies in each solvent, and is a minimum in the case of benzyl alcohol.

Effect of polymer concentration. The rate was fairly linear with time at polymer concentrations below 125 gm. l$^{-1}$ in most of the solvents fig. 12 and 13. But when the polymer concentration was increased above this, an initial slow rate, followed by

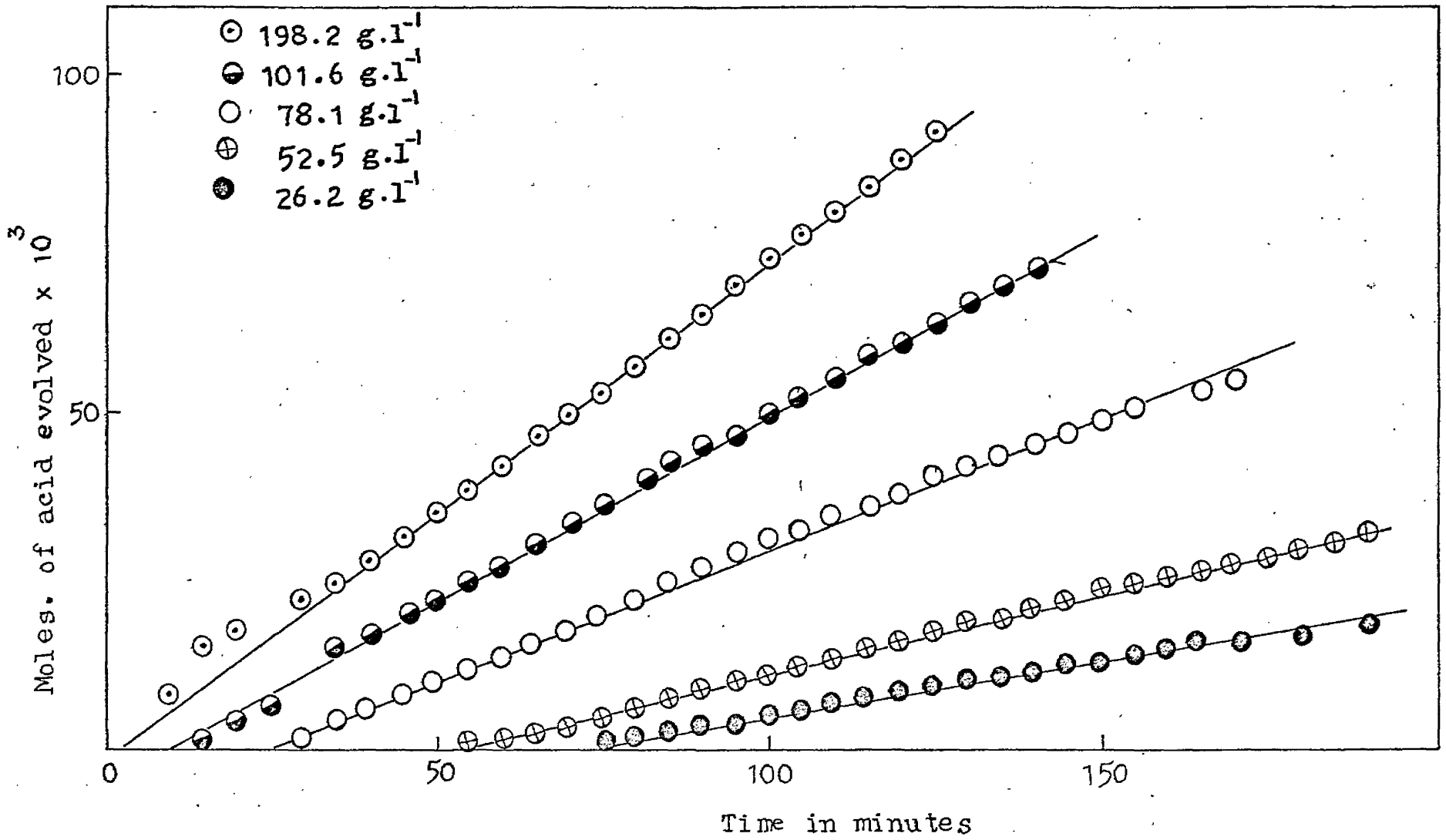



Fig. 12 The effect of concentration on dehydrochlorination of PVC ( Geon 111 ) in ethyl benzoate at 198° C

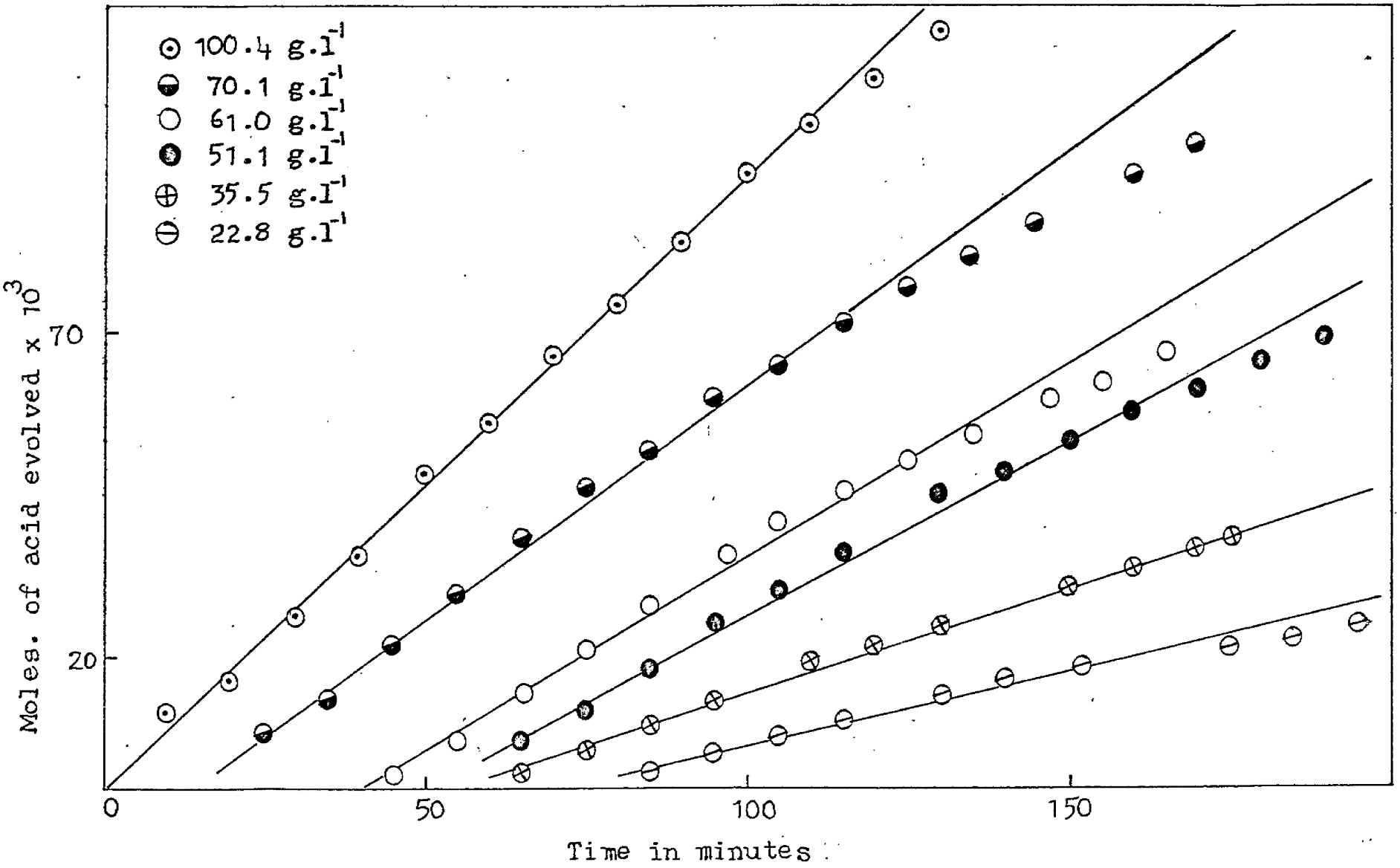


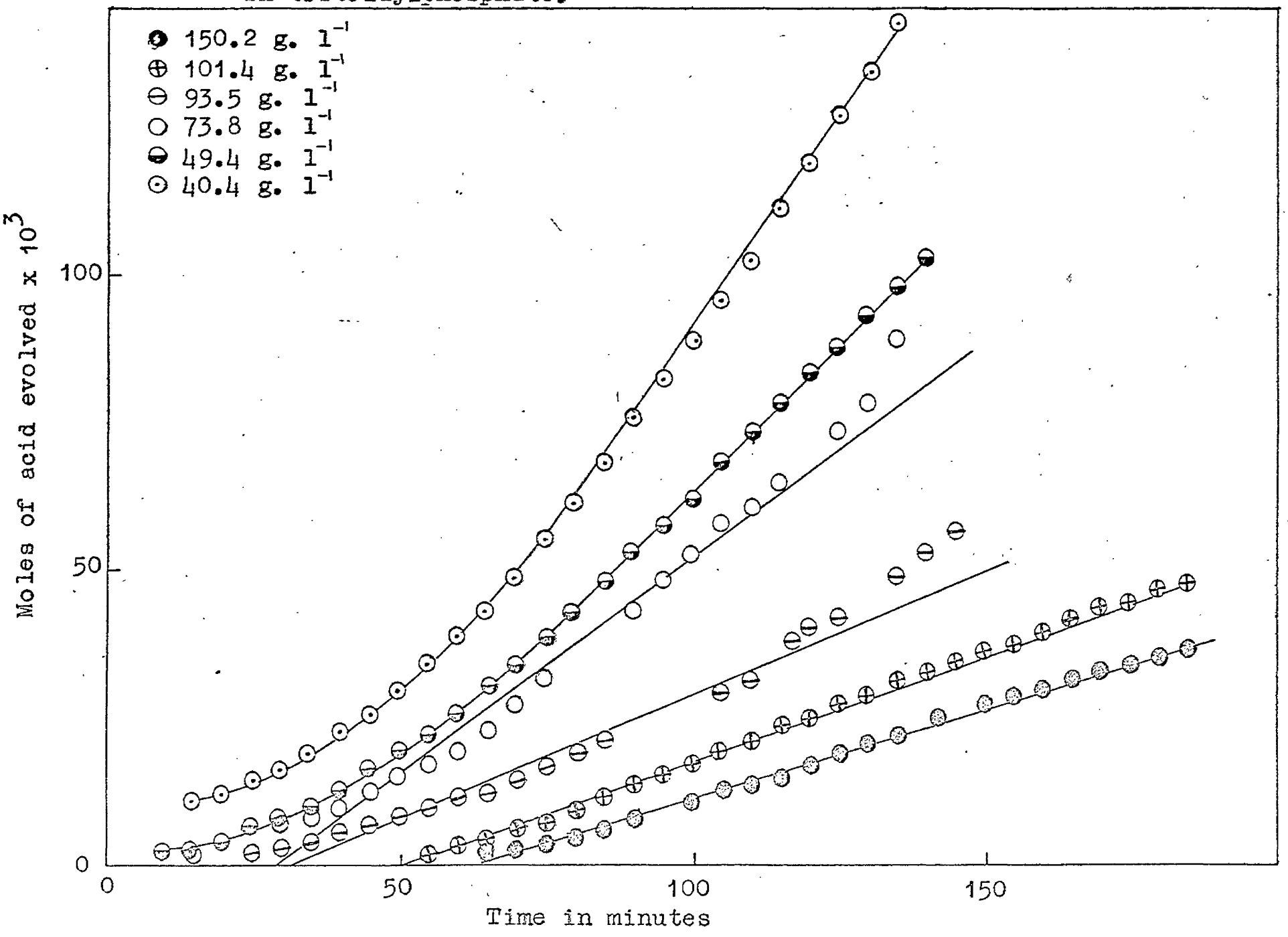

Fig. 13 Effect of concentration on the rate of dehydrochlorination of PVC in DOP at 212.6 °C.

an acceleration to attain the steady state was observed. This may be due to the increased viscosity of the polymer solution. In the initial stages the acid liberated under these conditions might be trapped due to the high viscosity of the solution. This might cause a decrease in the observed rate of dehydrochlorination initially. Later on, when the solution could hold no more acid an equilibrium might be reached between the trapped acid and the acid evolved. A steady rate of dehydrochlorination would then be observed. This phenomenon is more marked for viscous solvents, such as tritoluylphosphate. In this solvent at a concentration of 150 gm.$1000ml.^{-1}$ at 198°C this initial period of unsteady rate was upto 50 minutes (fig. 14).

In table 6 and fig.14B the dependence of rate on the polymer concentration is shown.

It is obvious, the amount of acid liberated per gm. of polymer is constant for any single solvent. However, at temperatures above this the yield of acid per gm. of polymer is not constant, as can be seen in table 7.

Fig. 14. Plot showing influence of polymer concentration on PVC degraded at 198°C in tritoluylphosphate.



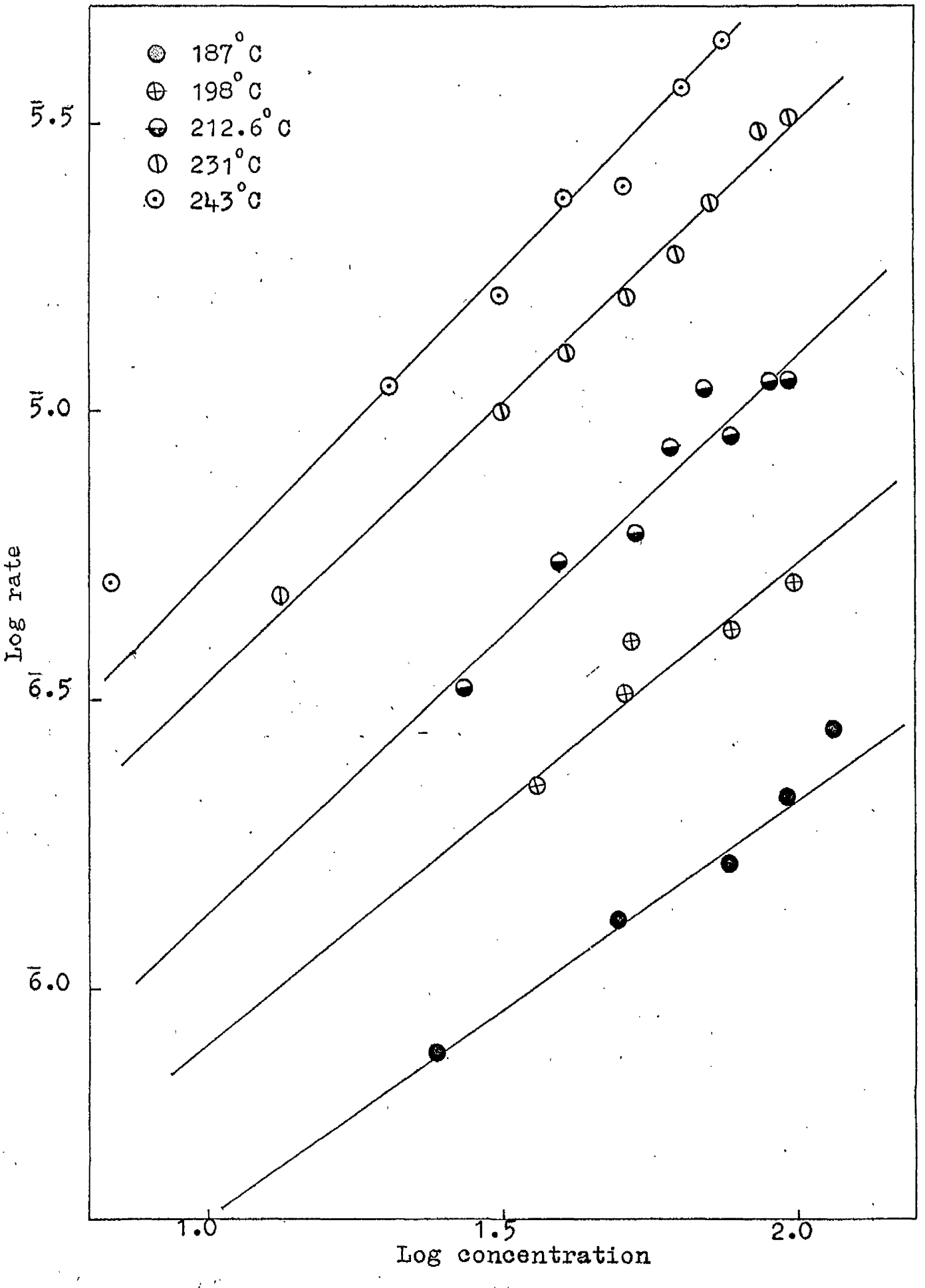



Fig. 14 ( B ) Dependence of rate of dehydrochlorination on polymer conc. in dicloronaphthalene.

Table 6

Dependence of the rate of dehydrochlorination on the polymer concentration for the pyrolysis of PVC in different solvents at 212.6°C.

| Solvent | dHCl/dt Moles of acid $l^{-1} sec^{-1}$ x $10^6$ | concentration. $gm.l^{-1}$ | Moles of acid $gm.^{-1} sec^{-1}$ x 10 |
|---|---|---|---|
| | 4.58 | 28.3 | 1.62 |
| thyl benzoate | 5.83 | 48.8 | 1.19 |
| | 9.00 | 76.2 | 1.18 |
| | 11.94 | 100.8 | 1.18 |
| | 3.33 | 27.8 | 1.19 |
| ichloronaphthalene | 6.11 | 53.5 | 1.14 |
| | 9.16 | 78.0 | 1.17 |
| | 11.11 | 91.9 | 1.20 |
| | 11.11 | 99.2 | 1.12 |
| | 3.85 | 22.8 | 1.69 |
| ioctylphthalate. | 5.19 | 31.5 | 1.65 |
| | 8.93 | 51.1 | 1.75 |
| | 9.90 | 61.0 | 1.62 |
| | 11.91 | 78.6 | 1.54 |
| | 11.02 | 39.6 | 2.78 |
| enzophenone | 12.16 | 43.2 | 2.81 |
| | 17.11 | 59.7 | 2.86 |
| | 22.22 | 71.2 | 3.12 |
| | 22.22 | 76.7 | 2.89 |
| | 5.00 | 17.8 | 2.81 |
| | 8.06 | 31.2 | 2.59 |
| ritoluylphosphate | 13.33 | 50.9 | 2.61 |
| | 22.00 | 78.7 | 2.79 |
| | 36.66 | 100.1 | 3.66 |

Table 7

Dependence of the rate of dehydrochlorination on the polymer concentration for the pyrolysis of PVC in different solvents at 243°C.

| Solvent | dHCL/dt Moles of acid $l^{-1} sec^{-1}$ x $10^6$ | concentration $gm.l^{-1}$ | Moles of acid $gm.^{-1} sec^{-1}$ x 10 |
|---|---|---|---|
| Dichloronaphthalene | 5.000 | 7.00 | 7.142 |
| | 11.110 | 20.50 | 5.41 |
| | 15.833 | 31.50 | 5.025 |
| | 23.33 | 40.90 | 5.70 |
| | 24.545 | 52.30 | 4.694 |
| | 36.66 | 64.4 | 5.69 |
| | 43.83 | 75.5 | 5.80 |
| | 63.33 | 91.6 | 6.91 |
| Dioctylphthalate | 14.940 | 26.9 | 5.55 |
| | 19.041 | 31.6 | 6.03 |
| | 25.83 | 47.6 | 5.42 |
| | 55.55 | 65.4 | 8.49 |
| | 48.076 | 75.3 | 6.381 |
| | 62.22 | 77.0 | 8.08 |
| | 76.00 | 92.0 | 8.26 |
| Tritolylphosphate | 15.470 | 10.1 | 15.34 |
| | 19.871 | 11.6 | 17.11 |
| | 52.66 | 24.7 | 21.39 |
| | 63.88 | 32.8 | 19.47 |
| | 90.00 | 52.1 | 17.27 |
| | 213.33 | 73.5 | 29.01 |
| Benzophenone | 20.00 | 13.9 | 14.39 |
| | 52.38 | 27.2 | 19.25 |
| | 113.33 | 44.7 | 25.8 |
| | 136.66 | 48.0 | 28.42 |
| | 155.55 | 61.9 | 25.13 |
| | 240.83 | 89.3 | 26.93 |

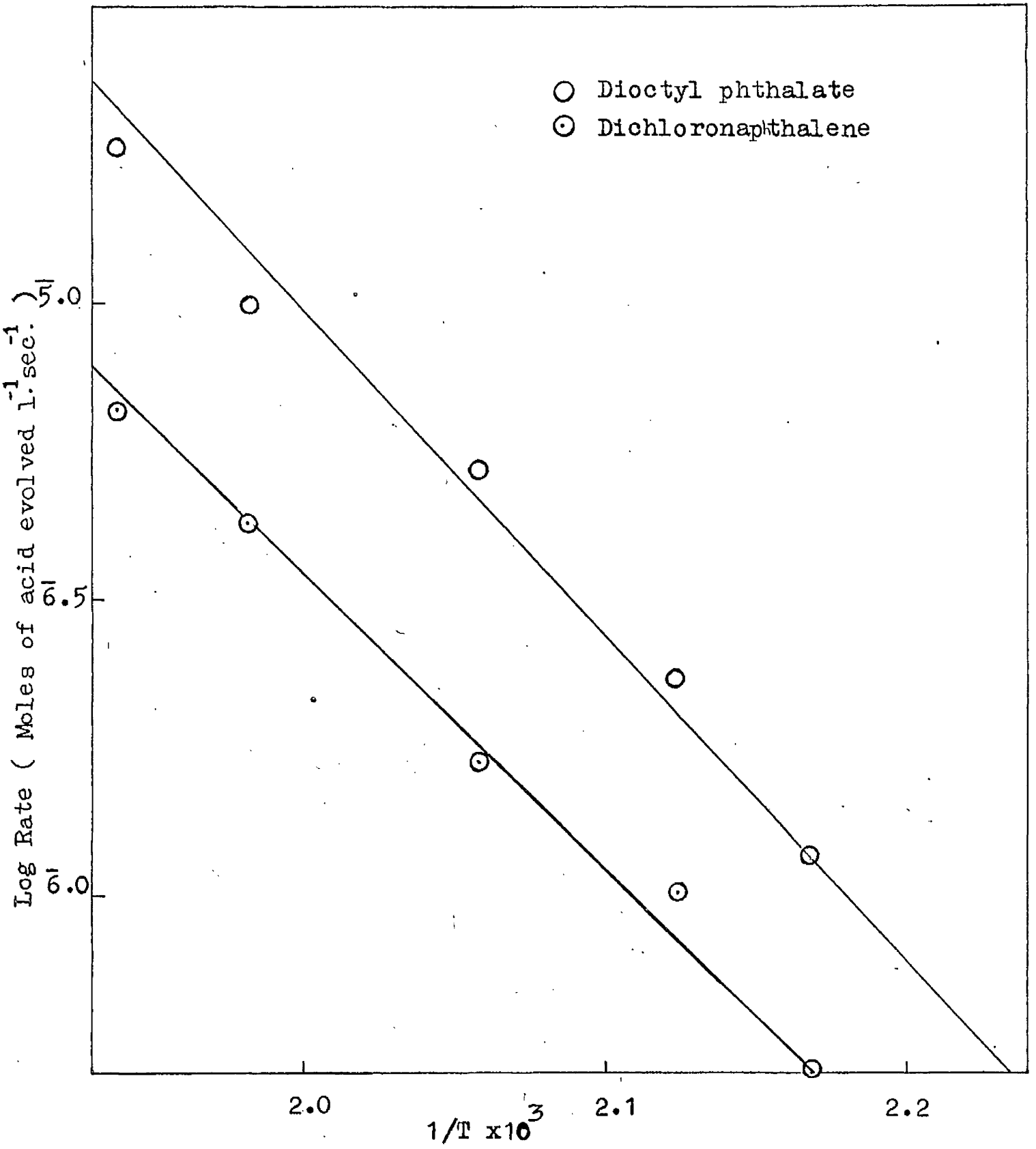



Fig. 15 Typical Arrhenius Plots for the dehydrochlorination of PVC ( Geon 111. )

Effect of temperature. Rates of dehydrochlorination of PVC were determined at five temperatures in benzophenone, dichloronaphthalene, dioctylphthalate and tritoluylphosphate i.e. 187°C, 198°C, 212.6°C, 231°C and 243°C. As the boiling point of ethylbenzoate was 212.6°C and of benzyl alcohol 205°C, the rates in these solvents were determined only at three temperatures.

The activation energy for dehydrochlorination was determined by plotting log of the rate against the reciprocal of the absolute temperature at two different polymer concentration (fig. 15). The slope of the resulting line yielded the activation energy.

Table 8

Activation energies for the dehydrochlorination reaction in different solvents.

| Solvent | Activation Energy ($k.cal.mole^{-1}$) |
|---|---|
| ethyl benzoate | $17.42 \pm 1$ |
| dioctylphthalate | $26.13 \pm 0.8$ |
| dichloronaphthalene | $24.18 \pm 1.1$ |
| benzyl alcohol | 23.03 |
| benzophenone | $30.63 \pm 0.3$ |
| tritoluylphosphate | $31.15 \pm 0.2$ |

Degradation of PVC fractions. Dehydrochlorination of few PVC fractions, obtained by fractionation of commercial polymer as described in Chapter 2, was also investigated. The fractions were degraded in dioctylphthalate and at 198°C. The results of such investigations are given in Table 9.

Table 9

Dehydrochlorination of few PVC fractions at 198°C in dioctylphthalate

| Fraction | Rate of dehydrochlorination Moles of acid $l^{-1} sec^{-1} \times 10^6$ | concentration $gm.l^{-1}$ | $[\eta]$ $dl.gm.^{-1}$ | Moles of aci $gm.^{-1} sec^{-1} \times 10^7$ |
|---|---|---|---|---|
| Whole polymer | 2.62 | 32.3 | 1.10 | 0.811 |
| | 4.89 | 72.2 | 1.10 | 0.677 |
| Fraction $F_2$ | 3.86 | 35.2 | 1.32 | 1.096 |
| | 5.06 | 75.45 | 1.32 | 0.670 |
| Fraction $F_4$ | 3.91 | 35.8 | 1.125 | 1.092 |
| | 4.00 | 64.85 | 1.125 | 0.616 |
| Fraction $F_7$ | 3.47 | 28.05 | 0.460 | 1.237 |
| | 4.16 | 56.4 | 0.460 | 0.737 |
| Fraction $b_1$ | 4.305 | 66.3 | 0.94 | 0.649 |

It is evident from table 9, that there is no significant variation in the rate of dehydrochlorination of different PVC fractions.

## Discussion

The rate of dehydrochlorination was slowest in the case of benzyl alcohol and was highest for benzophenone and tritoluylphosphate. This may be due to the form of the polymer in these solvents. Benzyl alcohol does not dissolve PVC at room temperature, but does so at a temperature of 178°C. Tritoluylphosphate on the other hand, has been used as a plasticiser for PVC and the solute solvent interaction would be much higher in such solvents, resulting in a highly extended polymer chain. The 'swelling factor' for a polymer solution could be defined as the ratio of the volume occupied by the polymer molecule to its actual molecular volume. In a good solvent, this factor is very large so variation in rate could perhaps be explained on the basis of polymer structure in these solvents.

Another explanation for the variability in the rate might be the difference in the dielectric constants of the solvents. The dielectric constant can be defined from the following equation.

$$\epsilon f r^2 = Q_1 Q_2 \qquad (5)$$

Where $Q_1$ and $Q_2$ are two charges separated by a distance r from each other, and f is the electrostatic force of attraction (or repulsion).

The $\epsilon$ values for all the solvents used here could not be obtained, but the values of some of these are mentioned below (values quoted from Handbook of Chemistry and Physics[64]).

Table 10

Dielectric constants for some solvents

| Solvents | $\epsilon$ | Temperature in $^{o}$Centigrades |
|---|---|---|
| Benzyl alcohol | 13.1 | $20^{o}$ |
| Ethylbenzoate | 6.02 | $20^{o}$ |
| Dibutylphthalate | 6.43 | $30^{o}$ |
| Tributylphosphate | 7.95 | $30^{o}$ |
| Tritoluylphosphate | 6.9 | $40^{o}$ |
| Benzophenone | 11.4 | $50^{o}$ |
| Cyclohexanone | 18.3 | $20^{o}$ |

The dielectric constants are temperature dependent and decrease with temperature. The value at other temperatures could be calculated provided $-\partial\epsilon/\partial T$ is known (where $\partial T$ is change in temperature). Calculations on this basis would give a value of $\epsilon$ for ethylbenzoate at $40^{o}$C as 5.978.

Looking at the above table, it becomes quite obvious that the variability of the rate could not be explained by the

differences in the dielectric constant of the medium. The rate of dehydrochlorination is high in benzophenone ($\epsilon = 11.4$) and low in benzyl alcohol ($\epsilon = 13.1$). There is significant difference in the dielectric constants of tritoluylphosphate and benzophenone, while the rates of dehydrochlorination are similar.

The rate of dehydrochlorination has been calculated as moles of acid evolved per litre per second. The dehydrochlorination of PVC has been reported as a first order process by Bengough and Sharpe[9]. The rate expression for a first order reaction of this kind is given by -

$$\text{moles of acid evolved lit.}^{-1}\text{sec.}^{-1} = k'C$$

where $k'$ = rate constant ($\text{sec.}^{-1}$)

$C$ = concentration in monomoles $\text{litre}^{-1}$

Concentration in monomoles $\text{litre}^{-1}$ is obtained by dividing the weight of polymer in $\text{gm.l}^{-1}$ by molecular weight of monomer

$$\therefore \quad k' = \frac{\text{Rate of dehydrochlorination}}{\text{monomoles litre}^{-1}}$$

The rate constant was evaluated, assuming the dehydrochlorination as first order process.

Calculated first order rate constants for the dehydrochlorination of PVC in different solvents at 212.6 °C

| Solvents | dHCl/dt Moles of acid $l^{-1}$ $sec^{-1}$ x $10^6$ | concentration monomoles $l^{-1}$ | $k' sec^{-1}$ x $10^6$ |
|---|---|---|---|
| | 4.58 | 0.4528 | 10.130 |
| Ethyl benzoate | 5.83 | 0.7807 | 7.470 |
| | 9.00 | 1.219 | 7.380 |
| | 11.94 | 1.613 | 7.410 |
| | 3.33 | 0.4440 | 7.494 |
| | 6.11 | 0.8560 | 7.137 |
| Dichloronaphthalene | 9.17 | 1.2480 | 7.345 |
| | 11.11 | 1.4700 | 7.558 |
| | 11.11 | 1.5870 | 7.000 |
| | 11.02 | 0.6334 | 17.400 |
| | 12.16 | 0.6911 | 17.590 |
| Benzophenone | 17.11 | 0.9552 | 17.900 |
| | 22.22 | 1.1400 | 19.500 |
| | 22.22 | 1.2280 | 18.090 |
| | 5.00 | 0.2847 | 17.740 |
| Tritoluylphosphate | 8.06 | 0.4993 | 16.140 |
| | 13.33 | 0.8143 | 16.370 |
| | 22.00 | 1.2590 | 17.480 |
| | 36.66 | 1.6020 | 20.910 |
| | 3.85 | 0.3648 | 10.540 |
| | 5.19 | 0.5040 | 10.300 |
| Dioctylphthalate | 8.93 | 0.8175 | 10.920 |
| | 9.90 | 0.9759 | 10.150 |
| | 11.91 | 1.2570 | 9.462 |
| | 15.64 | 1.606 | 9.738 |

So the k' values agreed fairly well with a first order reaction in all the solvents at this temperature. However, at temperatures above this, the value does no longer remain constant and it varies (Table 12).

Table 12

Calculated first order rate constants for the dehydrochlorination of PVC in different solvents at 243°C.

| Solvent | $\frac{d}{dt}$HCl/dt Moles of acid $l^{-1}$ $sec^{-1}$ | concentration monomoles $l^{-1}$ | Rate constant $k^1$ $sec^{-1}$ x $10^6$ |
|---|---|---|---|
| chloronapthtalene | 11.11 | 0.3280 | 33.870 |
| | 15.83 | 0.5040 | 31.420 |
| | 24.54 | 0.8368 | 29.330 |
| | 36.66 | 1.0300 | 35.420 |
| | 43.83 | 1.2080 | 36.290 |
| octylphthalate | 14.94 | 0.4304 | 34.710 |
| | 25.83 | 0.7615 | 33.910 |
| | 55.55 | 1.0470 | 53.090 |
| | 37.04 | 1.0590 | 34.970 |
| | 62.22 | 1.2320 | 50.510 |
| nzophenone | 20.00 | 0.1766 | 113.200 |
| | 52.38 | 0.4352 | 120.300 |
| | 113.33 | 0.7152 | 158.400 |
| | 240.83 | 1.4290 | 168.500 |
| itoluylphosphate | 19.87 | 0.1857 | 107.000 |
| | 52.66 | 0.3950 | 133.300 |
| | 87.87 | 0.6609 | 132.900 |
| | 90.00 | 0.8335 | 108.000 |
| | 126.66 | 0.9441 | 134.200 |

The average value of rate constants for different solvents at different temperatures are given in table 13.

Table 13

Calculated average value of first order rate constants for the dehydrochlorination of PVC in various solvents

| Solvent \ Temperature | 187°C | 198°C | 212.6°C | 231°C | 243°C |
|---|---|---|---|---|---|
| ethylbenzoate | 2.503 | 3.959 | 8.097 | - | - |
| benzyl alcohol | 0.268 | 0.479 | - | - | - |
| dichloronaphthalene | 1.568 | 3.772 | 7.953 | 20.259 | 36.232 |
| dioctylphthalate | 2.098 | 4.305 | 10.088 | 19.897 | 42.407 |
| tritoluylphosphate | 3.627 | 7.946 | 18.483 | 67.801 | 126.77 |
| benzophenone | 4.412 | 7.578 | 17.788 | 86.792 | 149.97 |

A plot of log rate vs. log concentration (fig. 14B) indicated a variation of $\pm$ 0.2 from the expected value of 1. The order was less than one at 187°C and greater than one at higher temperatures. Whether it is due to a change in the mechanism at higher temperature or just an experimental error is difficult to say. Guyot and Benvise[21] have reported the existence of two types of active centres for dehydrochlorination. They believe that in the temperature range of 150-190°C the unsaturated groups are the seat

for activation, but in temperature range of 200-250°C secondary activation of some irregular structures present in PVC takes place.

The rate constants for PVC fractions in dioctylphthalate at 198°C were also calculated and are reported in table 14.

Table 14

Calculated first order rate constants for the dehydrochlorination of fractions in dioctylphthalate at 198°C

| Fractions | dHCl/dt Moles of acid $l^{-1} sec^{-1} \times 10^6$ | concentration monomoles $l^{-1}$ | Rate constan $k^1$ $sec^{-1} \times 1$ |
|---|---|---|---|
| Whole polymer | 2.62 | 0.5168 | 5.078 |
| Whole polymer | 4.89 | 1.1550 | 4.240 |
| Fraction $F_2$ | 3.86 | 0.5700 | 6.790 |
| Fraction $F_2$ | 5.06 | 1.1910 | 4.250 |
| Fraction $F_4$ | 3.91 | 0.5720 | 6.830 |
| Fraction $F_4$ | 4.00 | 1.0370 | 3.850 |
| Fraction $F_7$ | 3.47 | 0.4500 | 7.700 |
| Fraction $F_7$ | 4.16 | 0.9020 | 4.160 |
| Fraction $b_1$ | 4.305 | 1.0500 | 4.100 |

The rate constants for whole polymer and its fractions which varied in intrinsic viscosity from 1.32 dl. $gm.^{-1}$ to 0.485 dl. $gm.^{-1}$ are very similar. These results will be discussed in detail in the following chapters (Chapter IV and VI).

Activation Energy in different Solvents.

There is a variation in the activation energy from solvent to solvent. It appears that solvents fall into three distinct groups (1) Solvent with a high activation energy (benzophenone and tritoluylphosphate) (2) Solvents with a moderate activation energy (benzyl alcohol, dichloronaphthalene and dioctylphthalate) (3) Solvents with low activation energy (ethylbenzoate). An average value of 23.2 k. cal. mole$^{-1}$ for PVC degradation has been reported by Bengough and Sharpe[9] in ethylbenzoate. This difference in our values may perhaps be attributed to a difference in the mode of preparation and in the molecular weight distribution of the two polymer samples.

The values reported in literature very enormously. Guyot et. al.[19] have reported a value of 20 k. cal. mole$^{-1}$ in the temperature range of 150 - 190$^{o}$C and 33 k. cal. mole$^{-1}$ between 200 - 250$^{o}$C. Stromberg[20] has reported a value of 30 k. cal. mole$^{-1}$, Grassie 28 k. cal. mole$^{-1}$, Arlman[16] 34 k. cal. mole$^{-1}$ and Talamini and Pezzin[10] 33 k. cal. mole$^{-1}$. Imoto and Otsu[8] have reported a value of 7.1 k. cal. mole$^{-1}$ and Talamini et. al.[12] 28 k. cal. mole$^{-1}$.

Our studies thus indicate that dehydrochlorination of PVC is influenced by the solvent used. The degradation of PVC in solution has also been studied by Goto and Fuji[65], but they

measured the changes taking place in the viscosity of the solution. Their result also indicate that the functional groups of the solvent affect the degradation. They concluded that the shorter the chain length of the substituent attached to the benzene nucleus the greater the occurrence of chain scission reactions. The solvents used were dimethylphthalate, diethylphthalate, dibutylphthalate and dioctylphthalate.

Jellinek[66] has studied the thermal degradation of polystyrene in solutionsof naphthalene and tetralin. The intrinsic viscosity dropped from 1.05 to 0.8 in tetralin while under the same thermal treatment it dropped to 0.4 in naphthalene. He attributed this change in reaction to a reaction similar to chain transfer. The thermal degradation of polystyrene in vacuum proceeds by the rupture of weak links. Subsequent degradation leads to the liberation of monomer units, and the reaction is stopped by some sort of termination reactions. Jellineck has suggested that tetralin formed radicals more easily by reacting with polymer radicals during degradation of polystyrene in solution than naphthalene.

It is, however, very difficult to explain our results on this basis as there is no obvious reason why chain transfer reactions with the various solvents should differ so markedly.

Another possibility is a type of ester interchange reaction between chlorine on polymer and the solvents. Such reactions are known to occur with salt but have not been reported for esters in the absence of catalyst. Bengough et. al.[72] have investigated the ester exchange reaction between cadmium acetate and PVC.

# CHAPTER 4

## Section A

## Studies of absorption spectra of degraded PVC

Conjugated polyene structures are produced during the degradation of PVC and this leads to the development of colour. Several investigators [32,38] have studied the effect of ionising radiation on PVC and have followed the post-irradiation effects by means of u.v. spectrophotometer. The reported absorption spectra obtained after subjecting PVC to ionising radiations are, however, inconsistent. Loy[36] reported a broad absorption line extending through and beyond both ends of visible region. Atchison[34,35] obtained a broad absorption band at 490 m $\mu$ and a series of small absorption maxima in the region of 350 - 500 m $\mu$.

These absorption studies have, however, so far not been extended to thermally degraded polymer. In the present work, we degraded the polymer in solution under vacuum, and followed the changes in the u.v. and visible absorption spectra at regular intervals of time.

### Experimental

Vacuum line was built in Pyrex glass and consisted of a series of vacuum taps and traps. The pumping system consisted of a

mercury diffusion pump, backed by a rotary oil pump. All taps were greased with Apiezon M grease. The cold traps containg dri-Kold-acetone mixture were placed immediately before and after the diffusion pump to prevent the volatile contaminants going into the pumping system. A vacuum of $10^{-4}$ mm. of mercury as indicated by a Pirrani Gauge was attained.

Spectrophotometer. A Perkin Elmer model 137 u.v. spectrophotometer was used for these investigations. The cell compartment of the spectrophotometer was modified for accomodating the long cells used for degradation studies.

The cells. Quartz cells connected to a B-10 Pyrex joint via a graded Quartz to Pyrex seal were used. A weighed quantity of polymer was placed in the cell and 4 ml. of solvent was added. The solution was degassed on the vacuum line. Three cycles of freezing, evacuating and thawing were performed. The cell was then sealed off at the constriction, and the solution was degraded in a vapour jacket at the required temperature. The cell was removed at regular intervals of time from the vapour jacket, cooled to the room temperature and the u.v. - visible region spectra were recorded. A matched 1 cm. cell containing the solvent was placed in the reference beam.

The solvents used for the degradation study were dioctylphthalate, tritoluylphosphate, ethylbenzoate, benzophenone, dichloronaphtha-

lene, benzyl alcohol, nitrobenzene and dimethylformamide.

We could not extend our investigation in the u.v. region of spectrum below about 350 m $\mu$ because most of the solvents absorb strongly in this region and thus sufficient light was not reaching the photomultiplier. Tetrahydrofuran has no appreciable absorption in this region, and this was used as a solvent for recording the spectra from 200 m u - 350 m $\mu$. The degraded polymer was precipitated by adding methanol and the precipitate was dissolved in THF. The polymer was precipitated again by pouring the THF solution in excess of methanol, filtered and dried. This twice precipitated polymer dissolved in THF was used for the investigations from 200 - 350 m $\mu$. The THF used in these measurements was always distilled freshly, because even the traces of peroxides gave a wrong spectra.

A low polymer concentration was used for the absorption studies (3-7 $g.l^{-1}$). The effect of temperature on polymer degradation was investigated in dioctylphthalate, otherwise in all other solvents the degradation was carried at 198°C.

## Results

The absorption studies revealed the existence of a series of characteristic bands independent of the solvent for PVC degraded at 198°C in dioctylphthalate, tritoluylphosphate, ethylbenzoate, benzophenone, benzyl alcohol and dichloronaphthalene. The peaks were at 364, 388, 414, 436, 458 and 480 m $\mu$.

Fig. 16. Absorption spectra of PVC degraded at 198°C in various solvents.

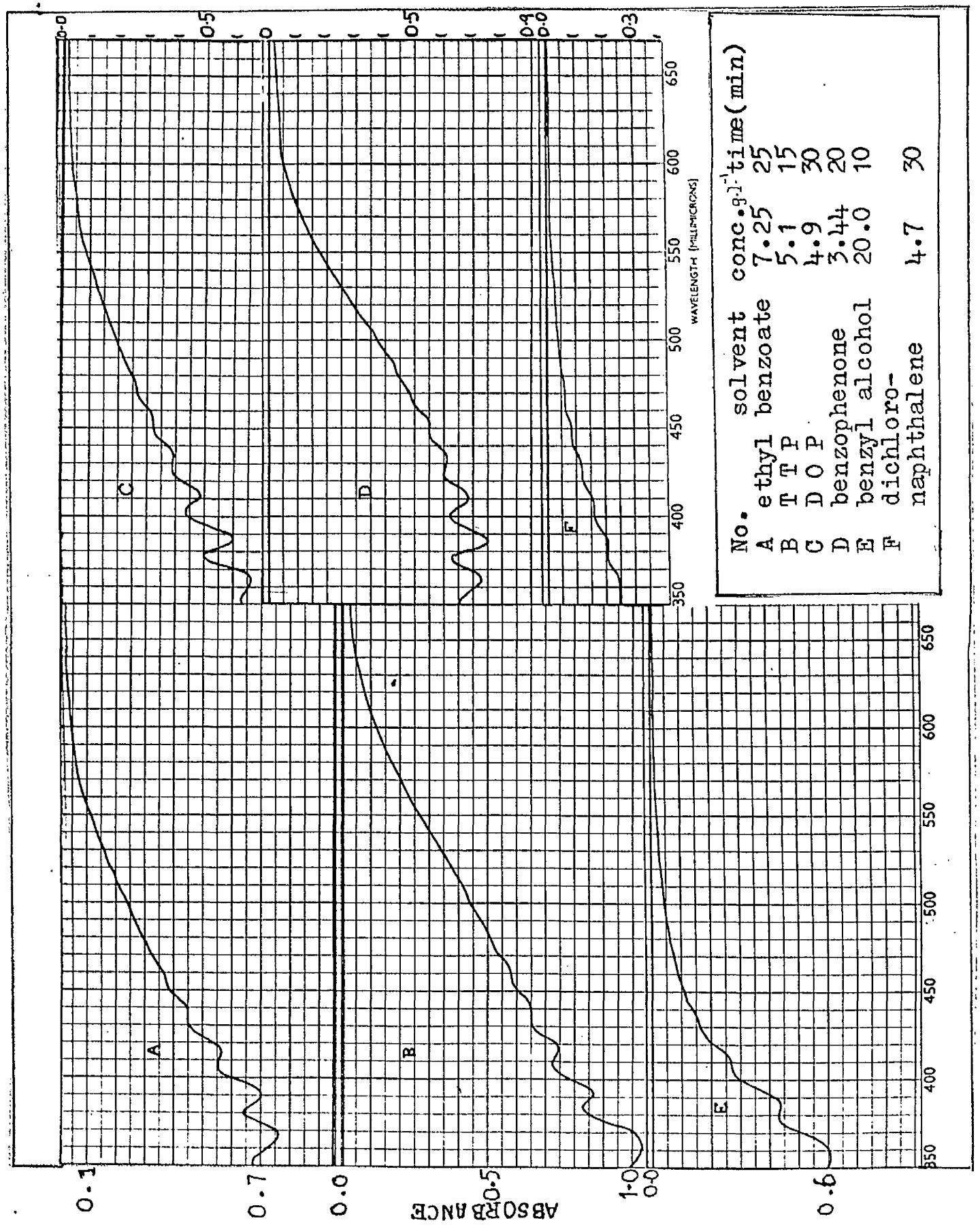
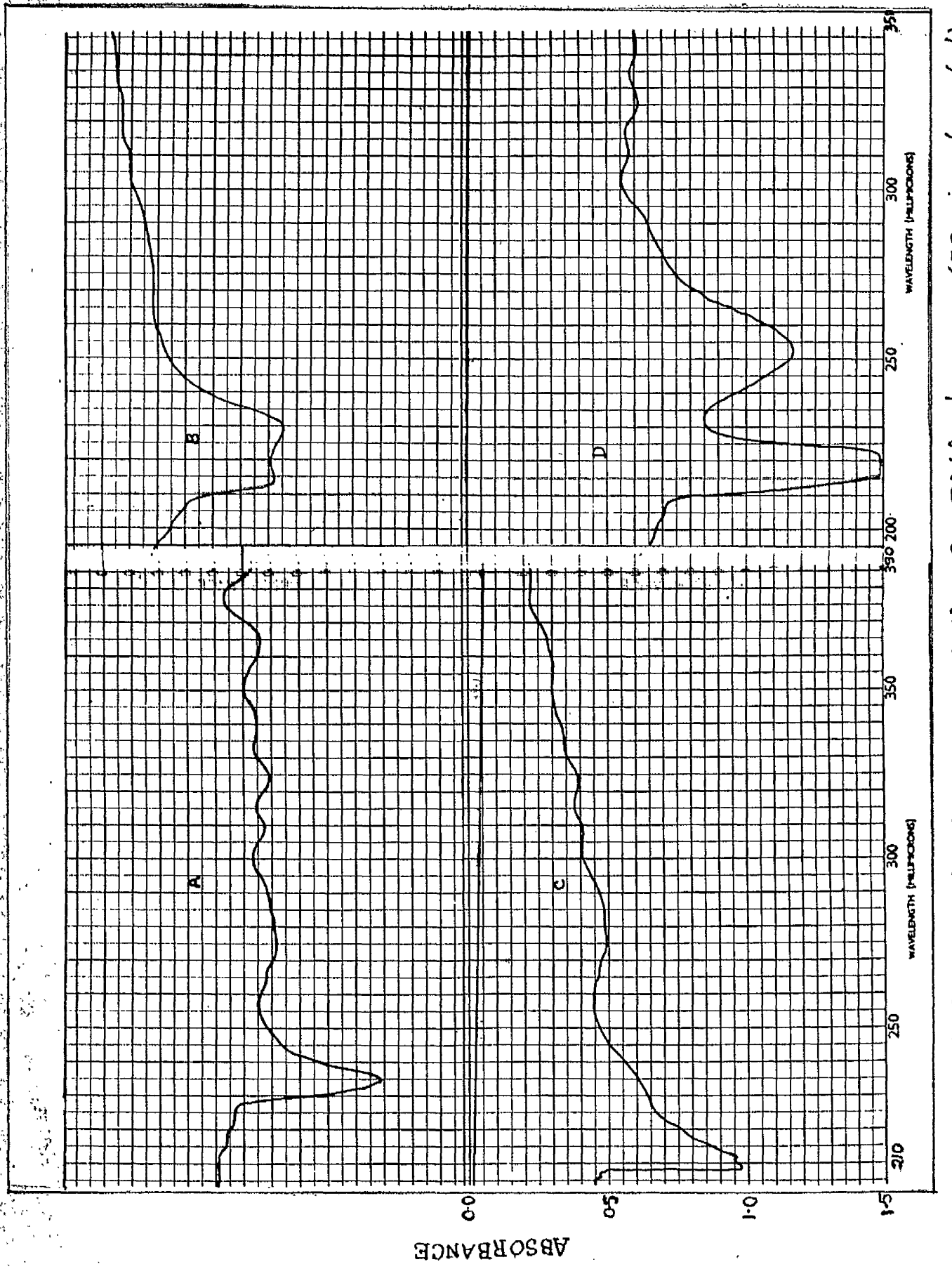
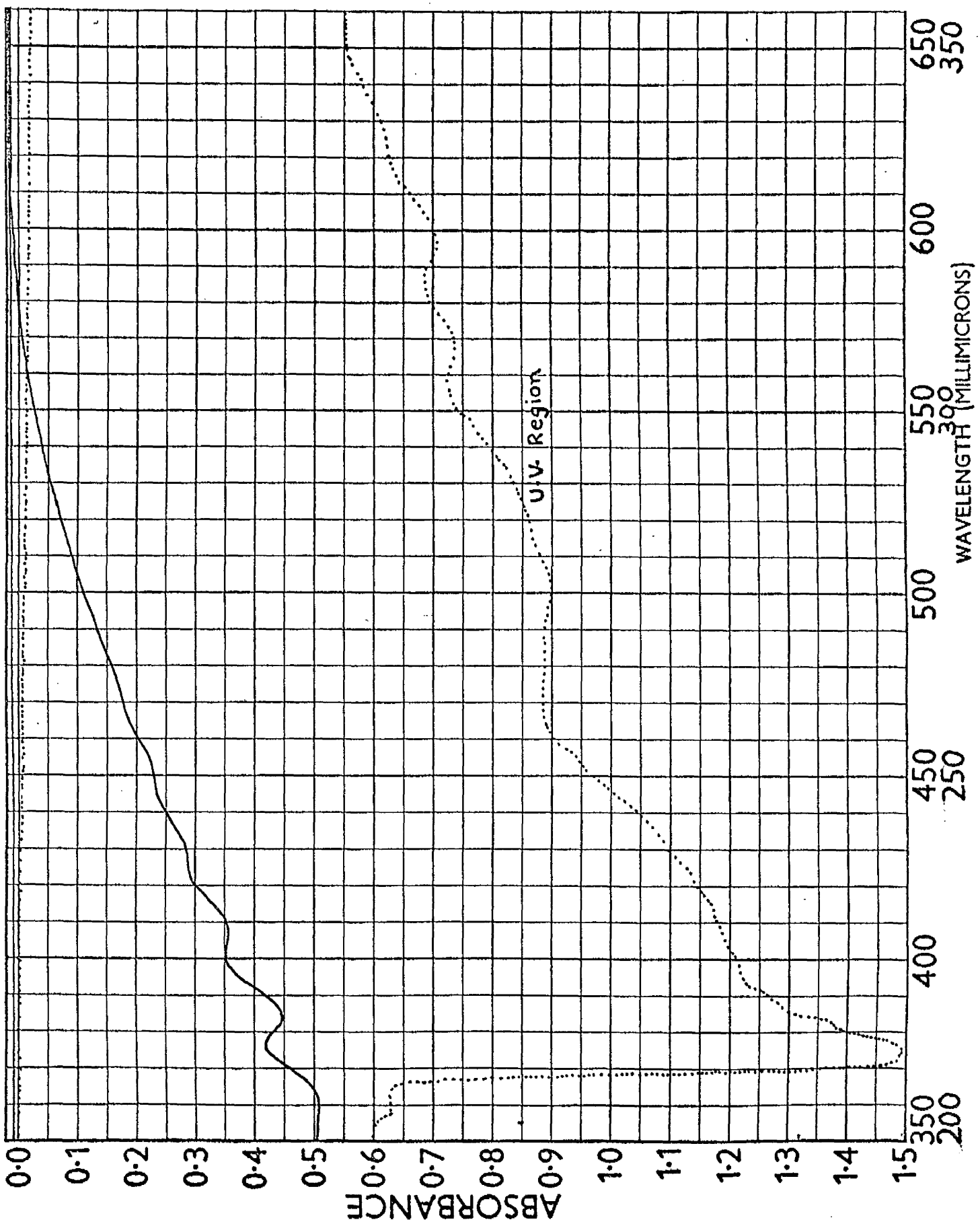


Fig. 17. Ultraviolet absorption spectra of PVC degraded at 198° C in various solvents. ( The spectra were recorded in tetrahydrofuran after pption of polymer. )




A = Ethyl Benzoate (10 mins. degraded) B = Dichlorobenzene (30 mins. degraded)
C = Dioctylphthalate (180 mins.degraded) D = Benzophenone (30 mins. degraded)

Fig. 18. Absorption spectra of PVC degraded for 30 minutes at 198°C in bulk.



A variation of ± 2 m $\mu$ was observed in different solvents (fig. 16). The spectra reported in fig. 16 for PVC degraded in benzophenone or dichloronaphthalene, were taken by precipitating the polymer, and dissolving the precipitated polymer in tetrahydrofuran. This was because benzophenone and dichloronaphthalene are solid at room temperature (m.p. 49°C and 37°C respectively) and so spectra could not be recorded in the presence of these solvents. It is quite clear from fig. 16 that absorption maximum in visible region is at 364 m $\mu$ or at 386 m $\mu$ (benzophenone) However, the precipitation and subsequent recording of spectra in the visible and ultraviolet region indicated that the absorption maxima was at 216 (± 2) m $\mu$ (fig. 17). The other peaks observed in this region were at 252, 275, 290, 310 and 325 m $\mu$. The absorption peaks in dichloronaphthalene were at 230, 275, 305, 322, and 335 m $\mu$. The peaks at 214 and 252 m $\mu$ and the relative heights of the peaks in this region are not very consistent. The long polyene chain is perhaps oxidised during precipitation yielding two or three double bonds compounds. The absorption at 216 or 252 would therefore depend upon the extent of oxidation. (It should be pointed out that butadiene, having two double bonds absorbs at 220 m $\mu$). To compare the results of solution degraded PVC with bulk polymer, a run was performed with bulk polymer. The absorption spectra of degraded bulk polymer in THF is shown in fig. 18. It is similar to the polymer degraded in different solvents.

Fig. 19. Influence of polymer concentration on the absorption spectra of PVC degraded for 10 minutes at 198° C in ethyl benzoate.

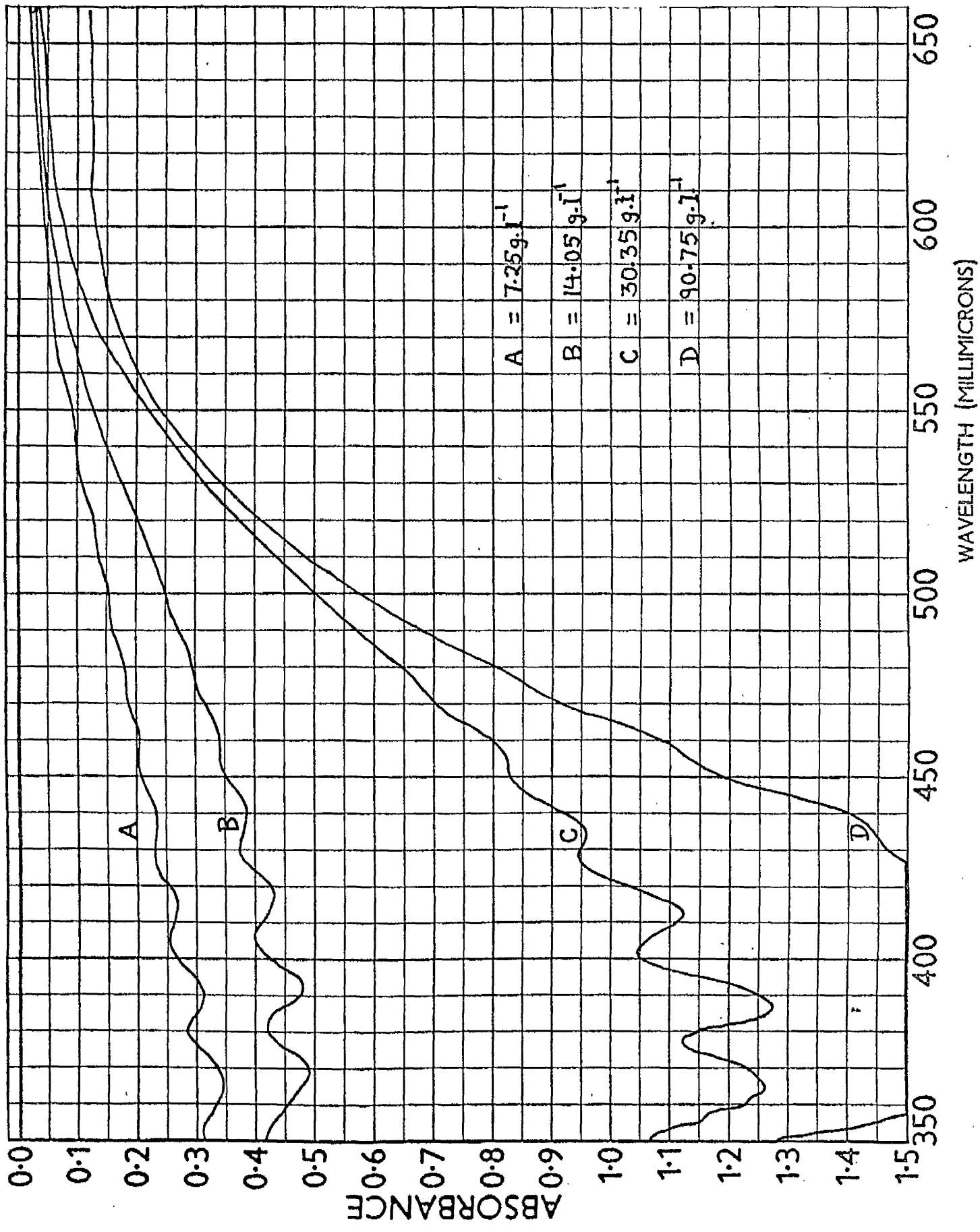


Fig. 20. Plot showing influence of polymer concentration on the absorbance at various wavelengths for PVC samples (ppted. polymer) degraded ten minutes at 198°C

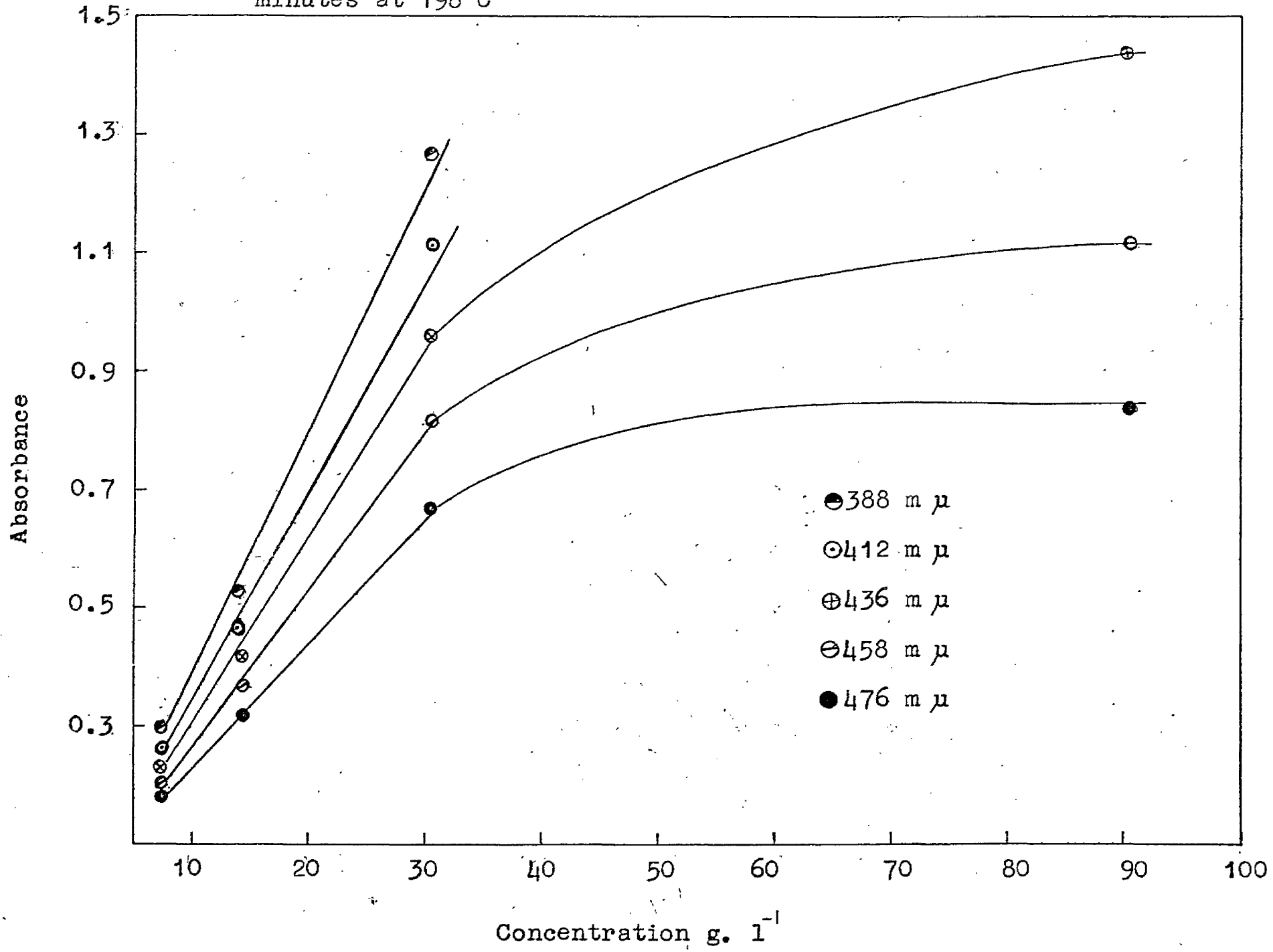
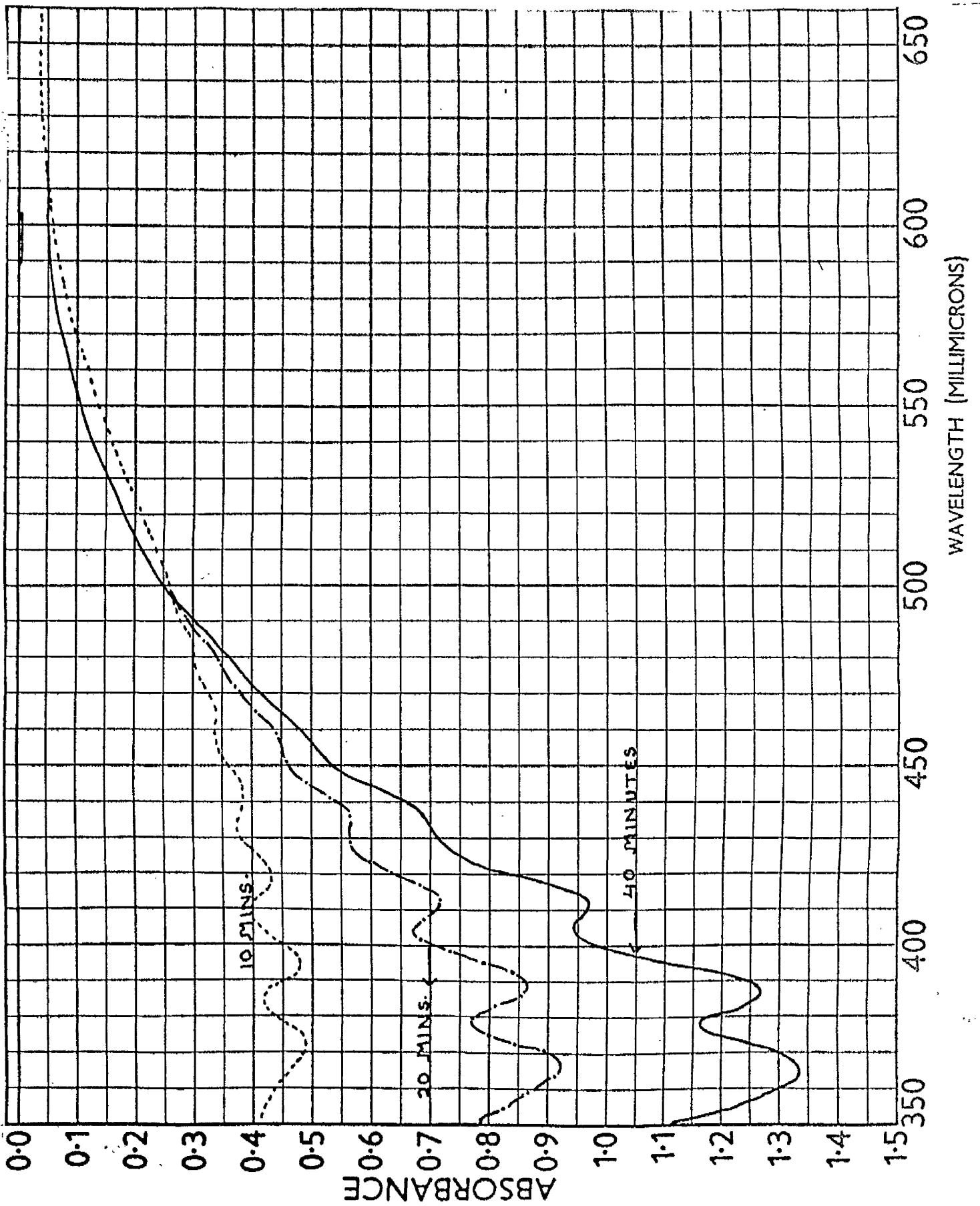


Fig.21 Absorption spectra of PVC solution (in ethyl benzoate, conc.= 14.05g.$l^{-1}$) showing the decay of longer chain polyenes with the increase in heating time.



Effect of polymer concentration upon degradation. The effect of polymer concentration was investigated using ethylbenzoate as the solvent. The concentration was varied from 7.25 $g.l^{-1}$ to 90.75 $g.l^{-1}$. The relative heights of peaks increased with increasing concentration, and there was a linear relationship between polymer concentration and optical density upto a concentration of 30 $g.l^{-1}$. The results are shown in fig. 19 and 20. The polymer was degraded for 10 minutes at 198°C. Fig. 20 indicates that there is a deviation from linear relationship in optical density and concentration, when the polymer concentration exceeds much beyond 30 $g.l^{-1}$.

Effect of heating time on degradation. Initially there was an increase in absorbance at all wavelengths in the visible region, (fig. 21), but after 20 - 30 minutes degradation the peaks at longer wavelengths started to decrease in height.

The relative heights of the peak (RH) with reference to peak at 366 m u is given by -

$$(RH) = \frac{\text{height of the peak at particular wavelength}}{\text{height of the peak at 366 m } \mu}$$

The RH of absorption peaks in different solvents started to decrease after some time (Table 15).

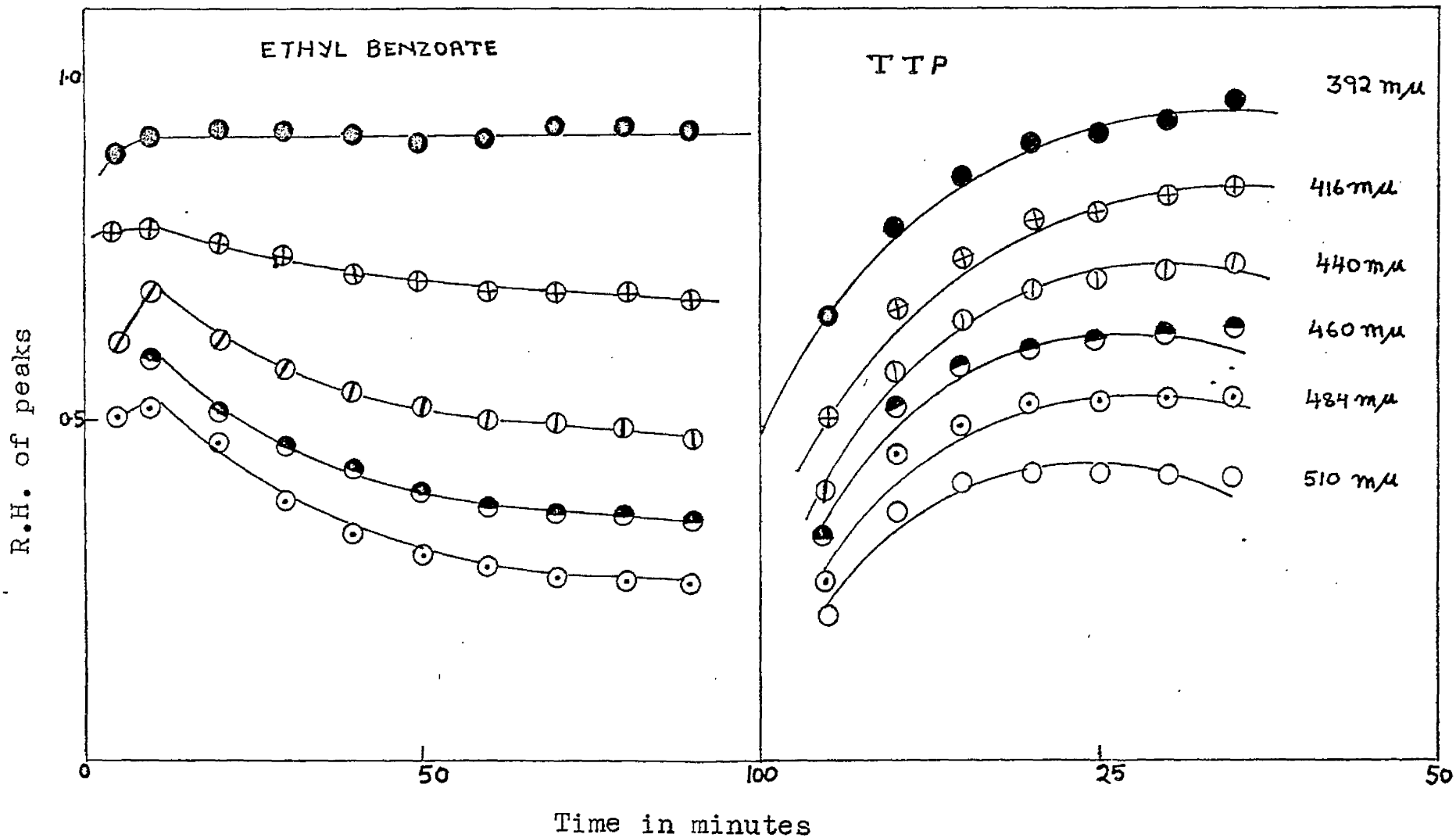



Fig.22 Plot showing decrease in relative heights (R.H.) of peaks with increasing time.

Fig. 23. Absorption spectra of PVC degraded in ethyl benzoate at 198°C, showing an increase in absorbance at longer wavelengths on prolonged heating.

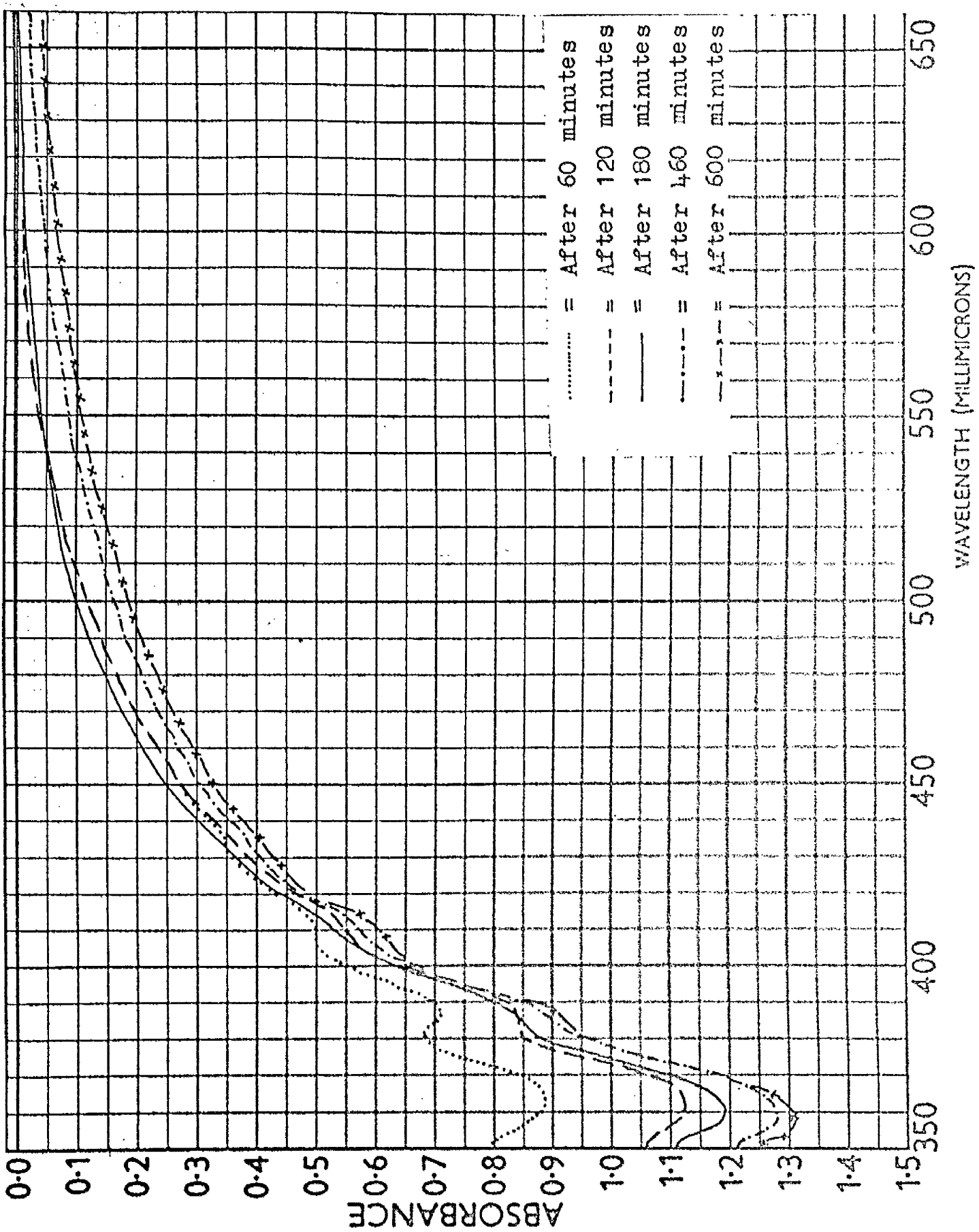


Fig.24. Effect of storage of PVC solution in ethyl benzoate (conc.14.05 g.$l^{-1}$) degraded 40 minutes at 198°C.

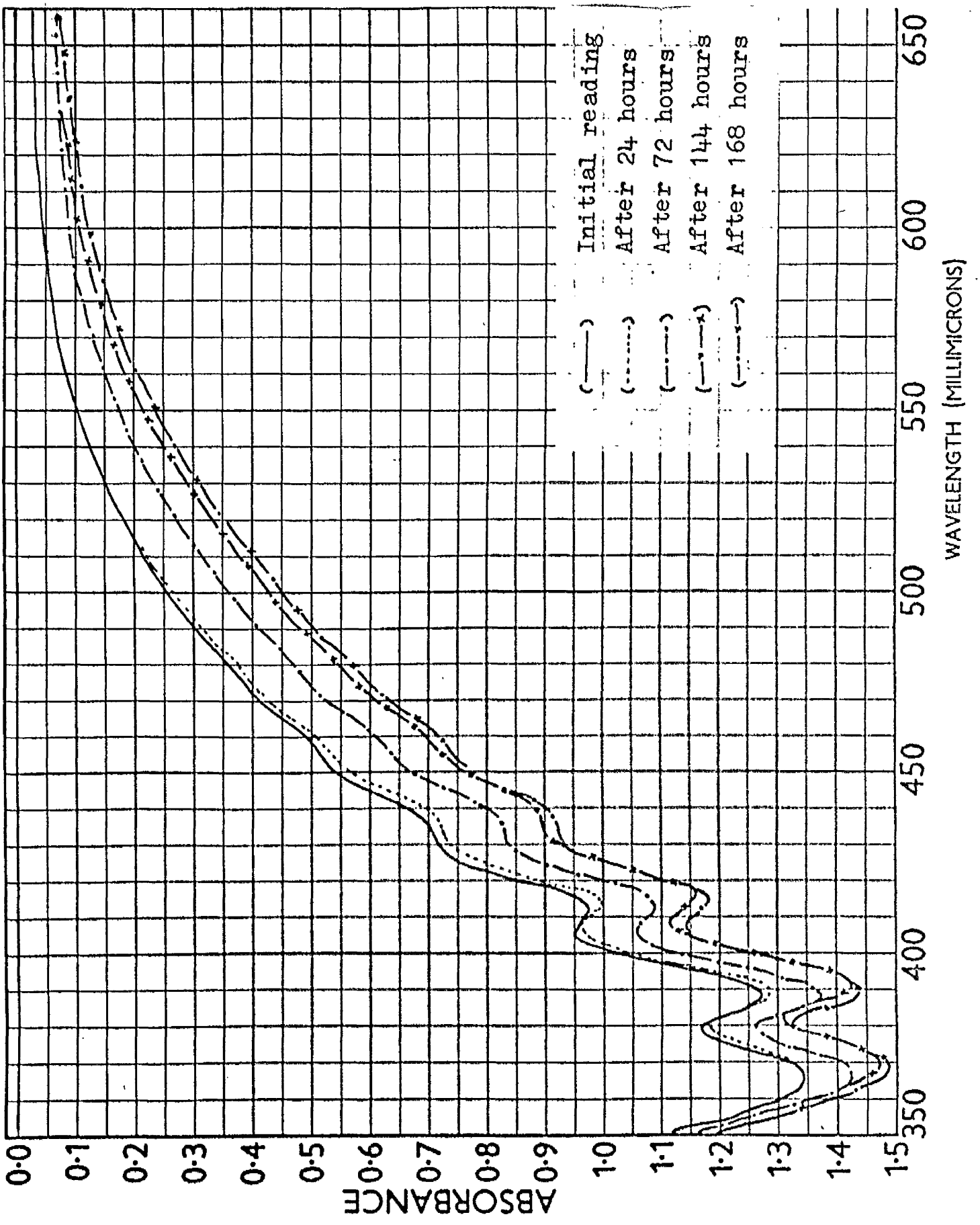


Fig.25. Effect of storage of PVC solution in tritoluylphosphate (conc.=1.975 g.l$^{-1}$) degraded 200 minutes at 198° C.

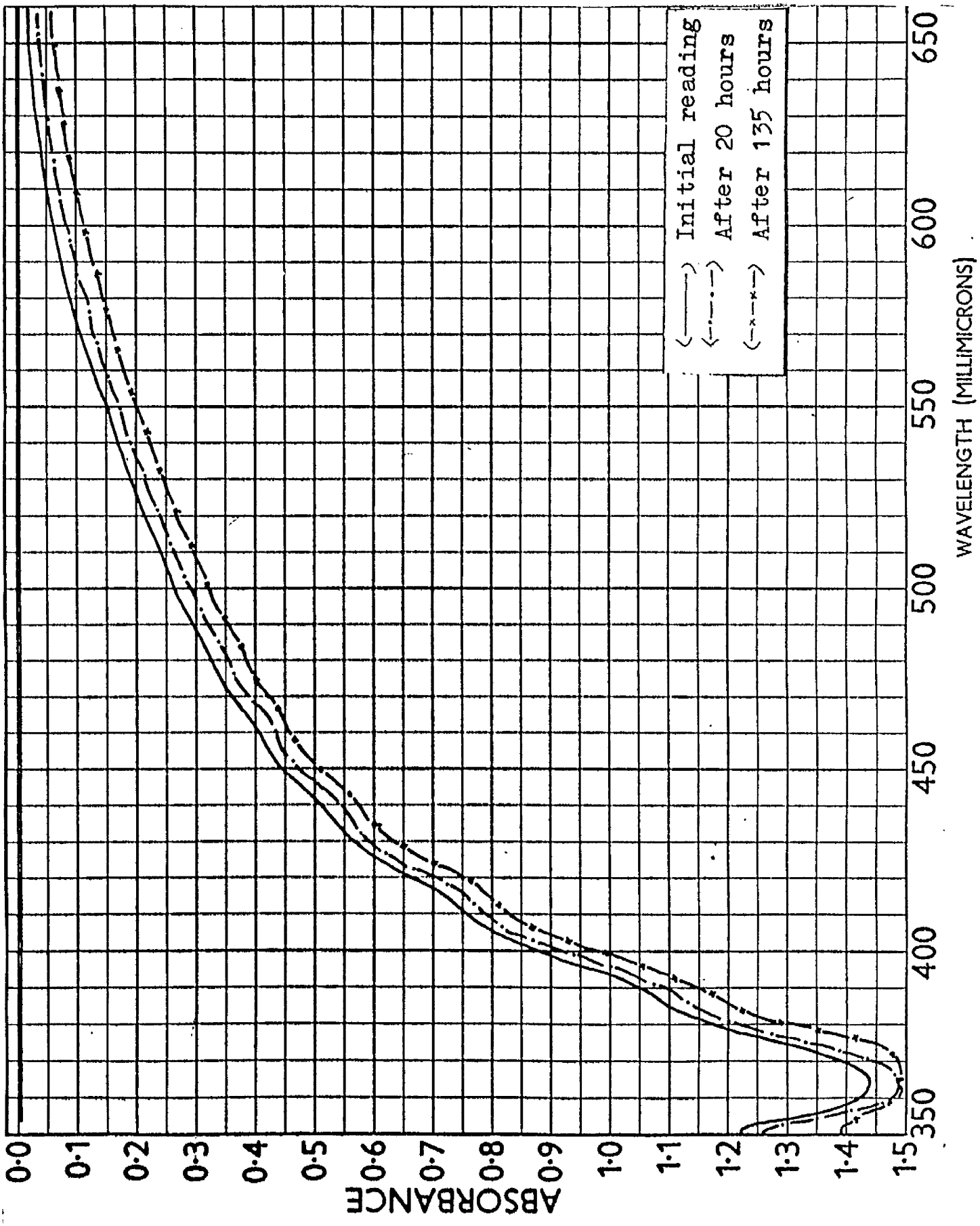


Table 15

The decrease in the relative heights of the absorption peaks in different solvents, as a function of time at 198°C

| Absorption peak \ Solvent | Ethylbenzoate 9.25 g.l$^{-1}$ | Dioctyl-phthalate 4.25 g.l$^{-1}$ | Tritoluyl-phosphate 1.975 g.l$^{-1}$ |
|---|---|---|---|
| 586 mμ | 60 mins. | 35 mins. | |
| 414 mμ | 20 " | 20 " | 40 mins |
| 436 mμ | 15 " | 15 " | 40 " |
| 458 mμ | 10 " | 15 " | 30 " |
| 480 mμ | 10 " | 15 " | 30 " |
| 570 mμ | - | 15 " | 15 " |

A plot of RH vs. heating time is shown in (fig. 22).

If the degradation was carried for a fairly long time (460 minutes) there was an increase in the absorption at longer wavelengths (fig. 23).

Effect of storage on the degraded solution at room temperature.

The storage of a degraded solution of PVC at room temperature in the dark caused an increase in the height of the peaks which was relatively higher at longer wavelengths than at lower wavelengths. The results of storage of this degraded PVC in ethylbenzoate, tritoluylphosphate and dioctylphthalate are shown in fig. 24 and 25.

Fig. 26. Effect of storage in air on the absorbance of a degraded PVC solution (in ethyl benzoate ).

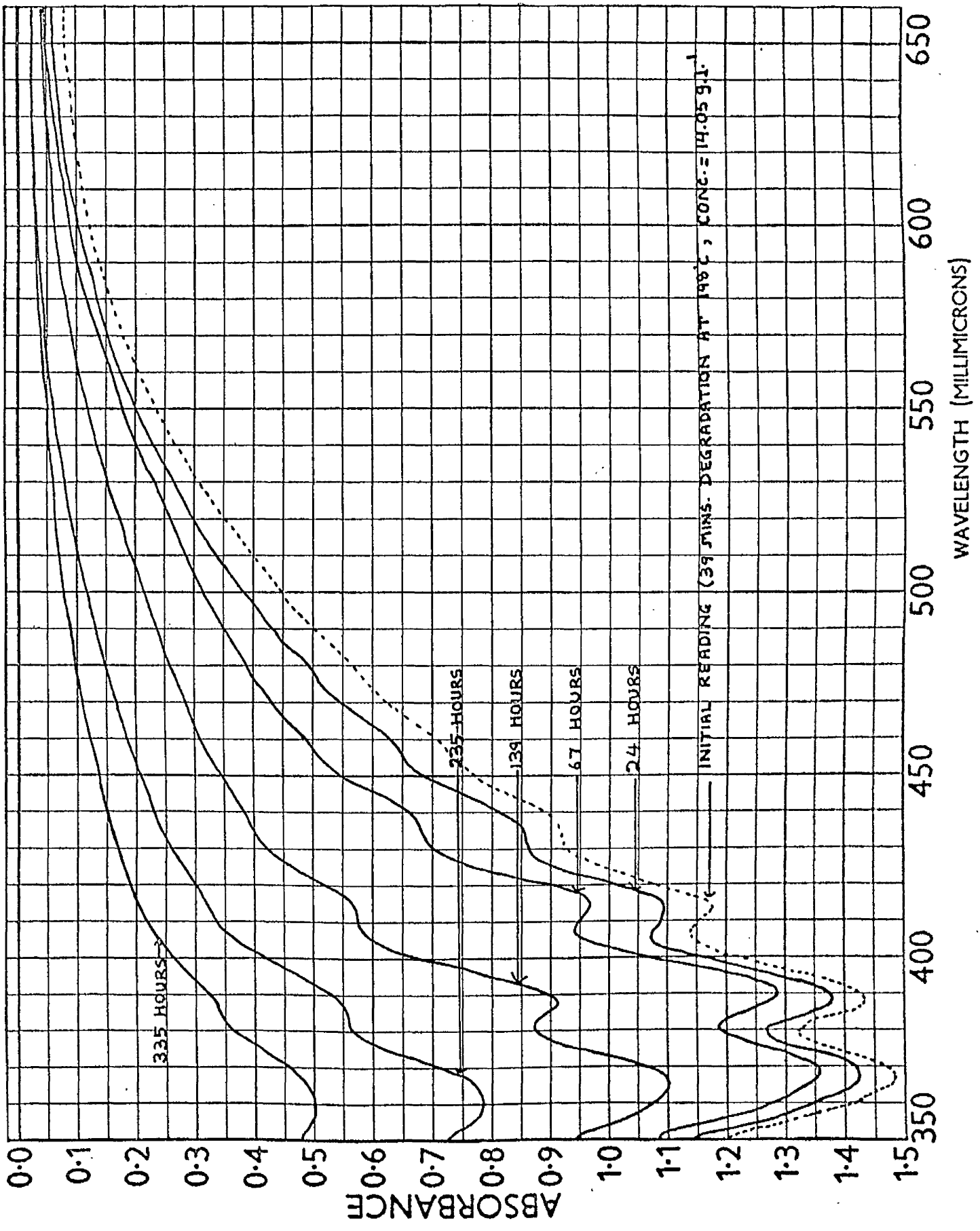


Fig.27. Absorption spectra of PVC degraded at 198° C in dioctylphthalate.

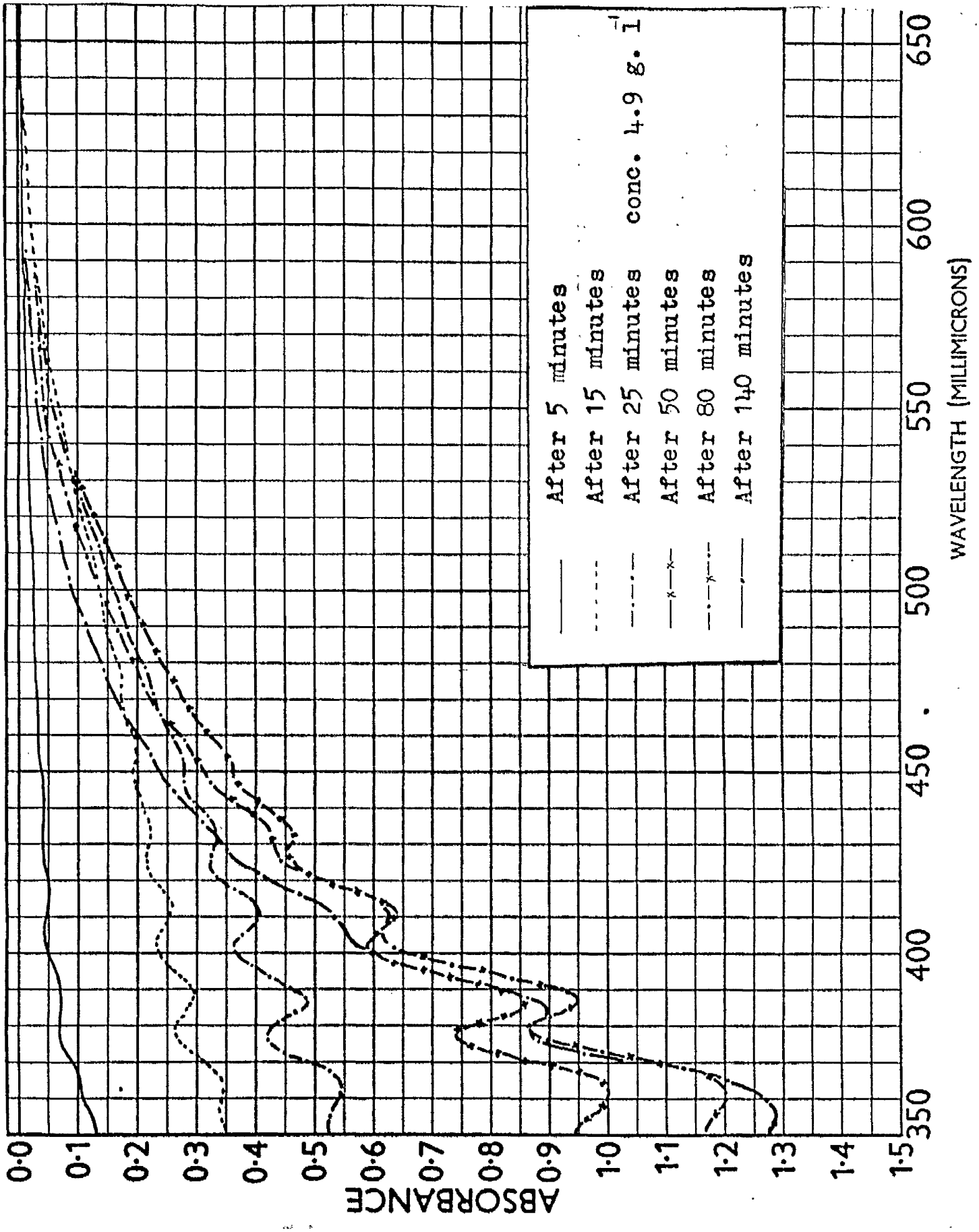


Fig.28. Absorption spectra of PVC degraded at 243° C in dioctylphthalate.

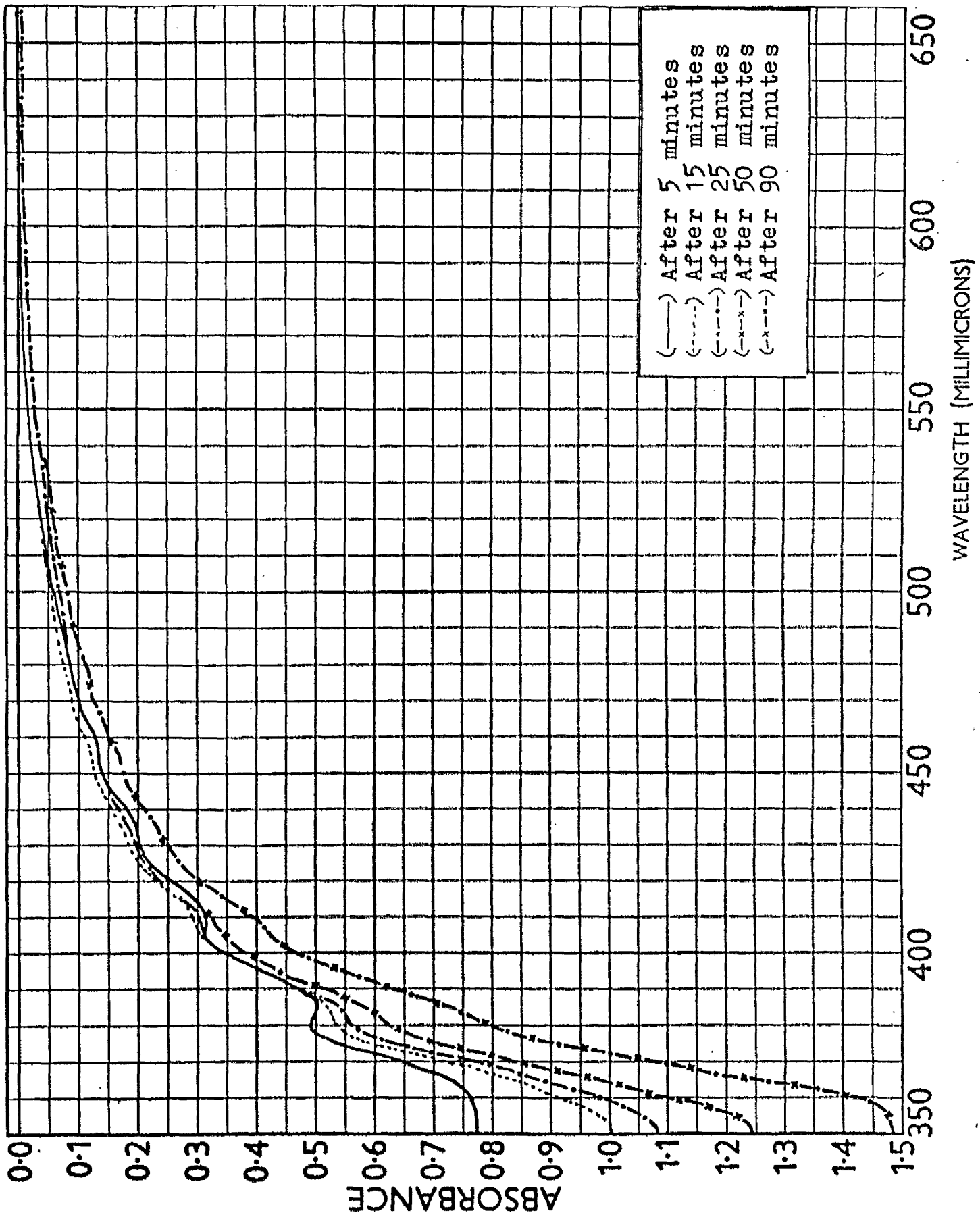


Fig. 29. Absorption spectra of PVC ( 4.00 $g.l^{-1}$ ) degraded at 212.6°C in dioctylphthalate.

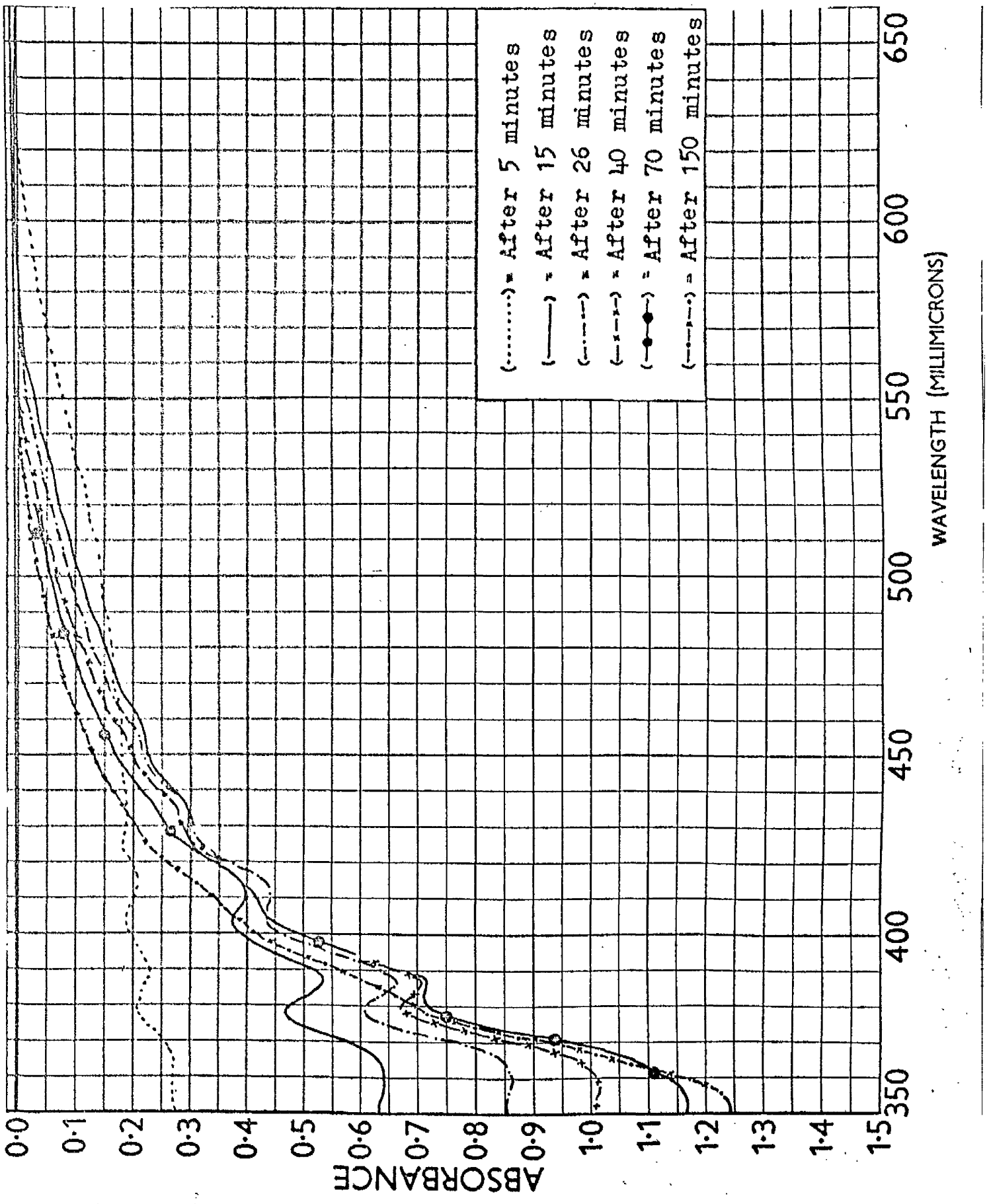
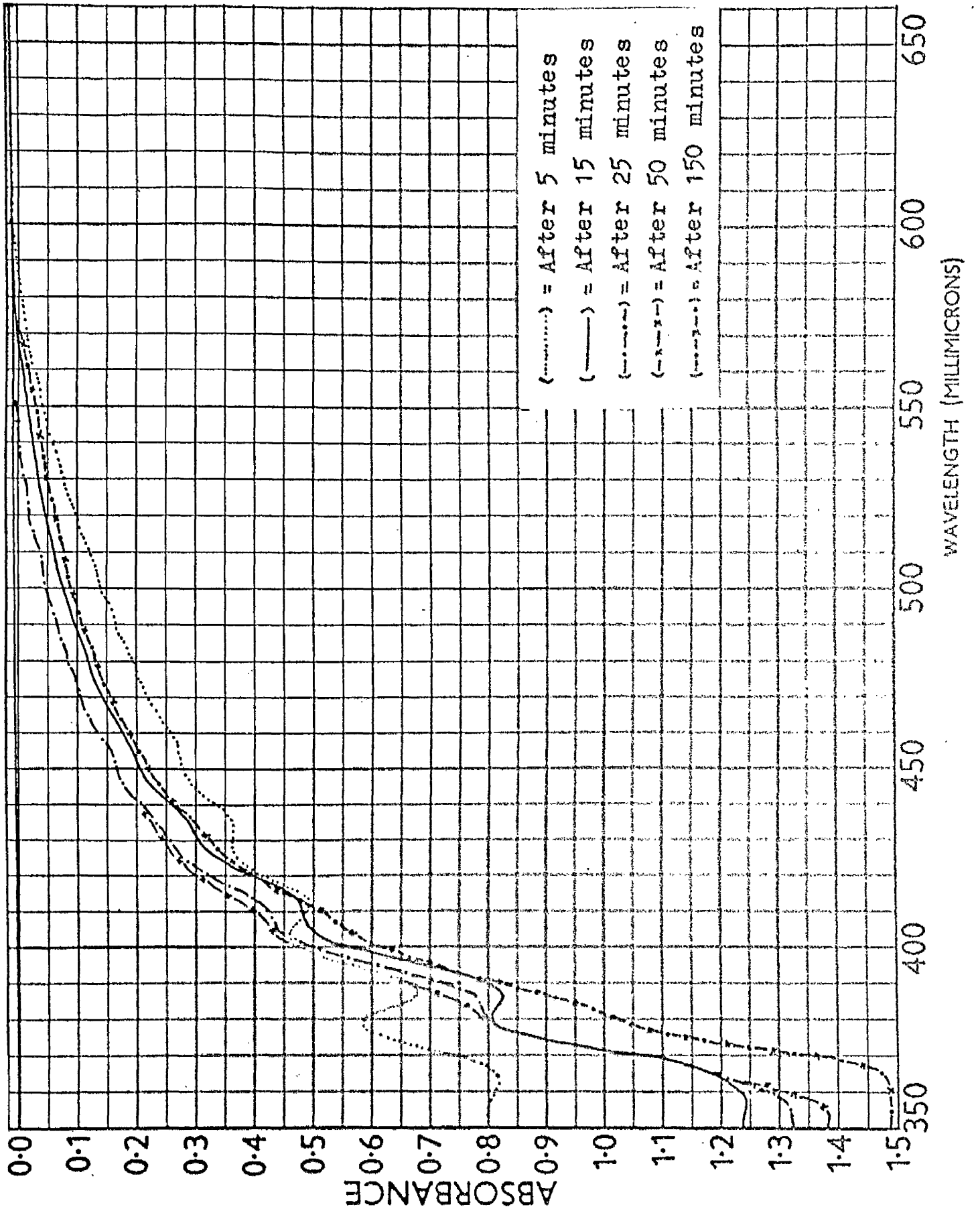


Fig. 30. Absorption spectra of PVC (4.05 g. $l^{-1}$) degraded at 231°C in dioctylphthalate.



Effect of keeping the degraded solution in air. The polymer solution, after an initial 39 minutes degradation in ethylbenzoat. (14.05 g. $l^{-1}$) when left open to the atmosphere, gradually became colourless [fig. 26]. The absorption bands at the higher wavelengths were the first to disappear. The fine nature of the peaks disappeared gradually as the peaks broadened.

Effect of temperature. The effect of temperature was investigated in dioctylphthalate at 198°C, 212.6°C, 231°C and 243°C. At 198°C there is an increase in the absorption band for the initial 30 minutes heat treatment, and peaks are formed at 364, 388, 412, 436, 458 and 476 m $\mu$. After this a gradual decrease in the absorption at higher wavelengths take place and after 140 minutes of degradation, only three peaks are left i.e. at 358 m $\mu$, 386 m $\mu$ and 410 m $\mu$ (fig. 27). On the other hand, at 243°C the peaks are never so well defined as at 198°C and after 20 minutes of degradation peaks at 354 m $\mu$, 384 m $\mu$ and 412 m $\mu$ remain (fig. 28). The absorption spectra at 212.6°C and 231°C are intermediate between these two extremes (fig. 29 and 30). By plotting the optical density at a particular wavelength vs. the heating time, an idea about the rate of increase of conjugated polyene chain may be obtained. Such plots are shown in fig. 30 - 34. Thus the peak at (fig. 31) 364 m $\mu$

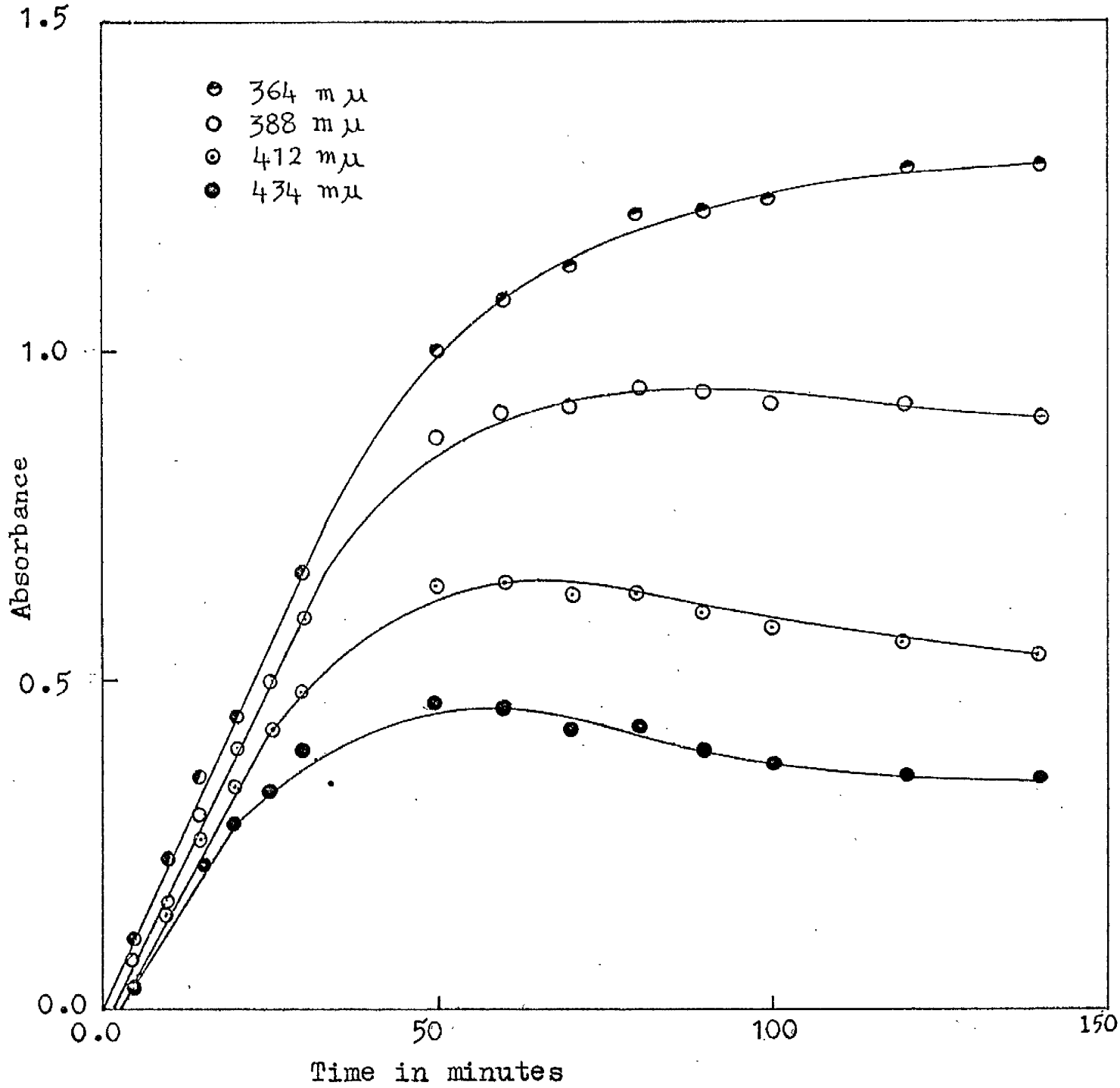



Fig.31.Effect of heating time on the absorbance at various wavelengths for PVC degraded at 198°C in DOP.

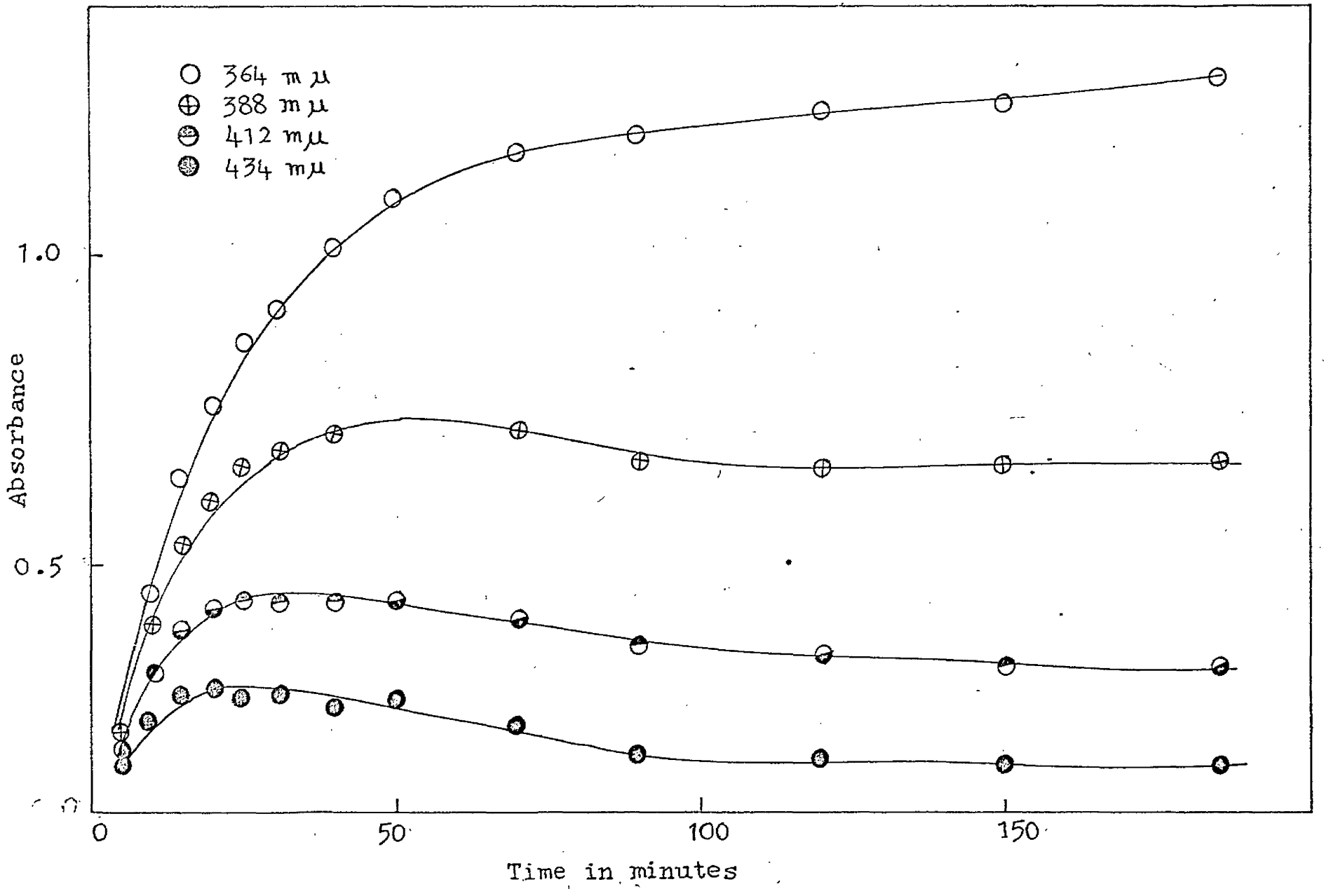



Fig.32 Effect of heating time on the absorbance at various wavelengths for PVC degraded at 112·6° C in DOP.

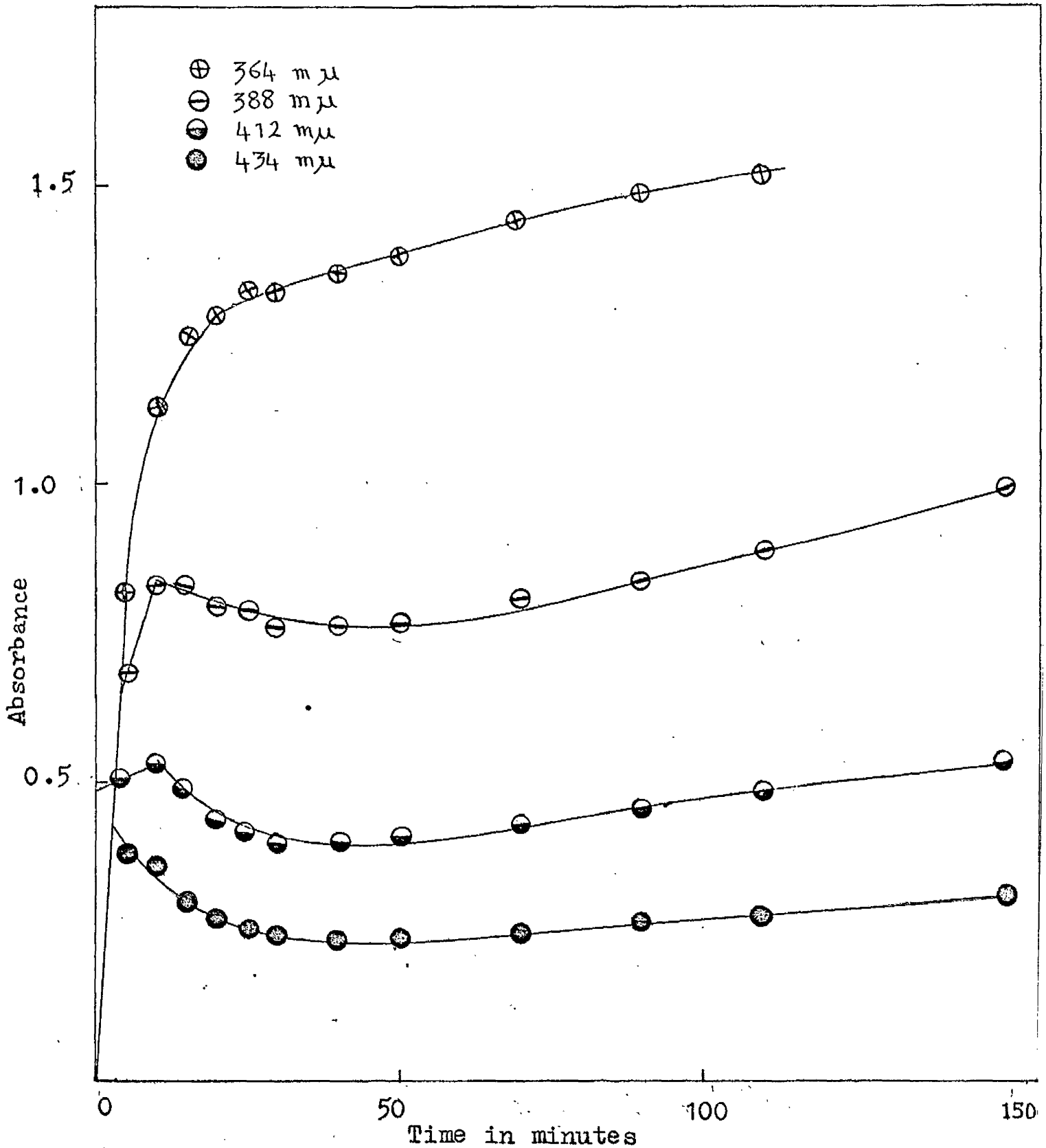



Fig. 33 Effect of heating time on the absorbance at various wavelengths for PVC degraded at 231° C in DOP.

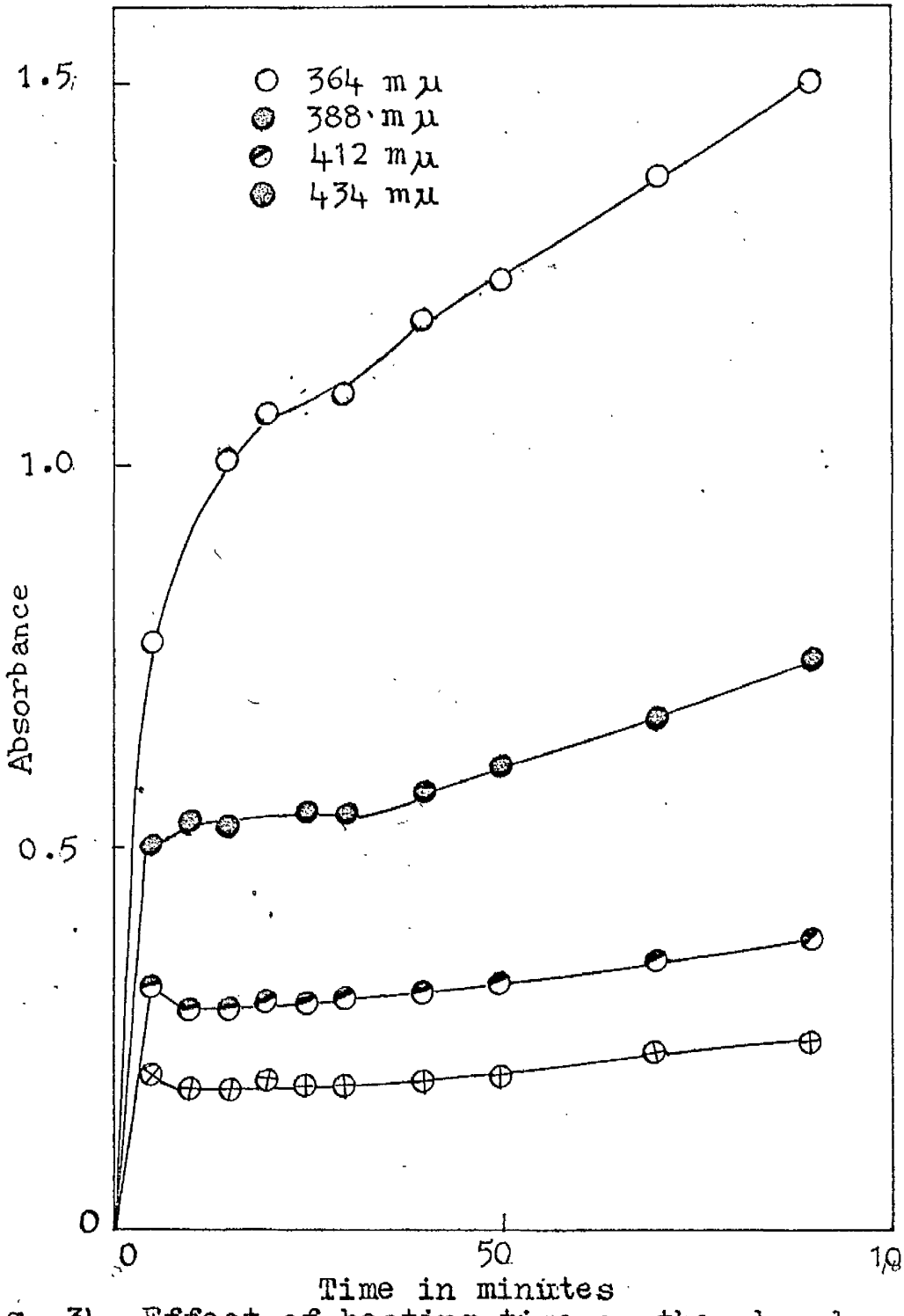



Fig. 34. Effect of heating time on the absorbance at various wavelengths for PVC degraded at 243 C in DOP.

increases for first 30 minutes at a faster rate and then gradually the rate falls off. At 243°C, the initial rate is very fast for first 5 minutes and then it decreases, and rate again increases after 40 minutes of thermal treatment. The activation energies have not been calculated because the rate of increase in absorption peaks is very fast at high temperatures. The spectra of initial heating time should therefore be recorded consistently to work out the correct rate.

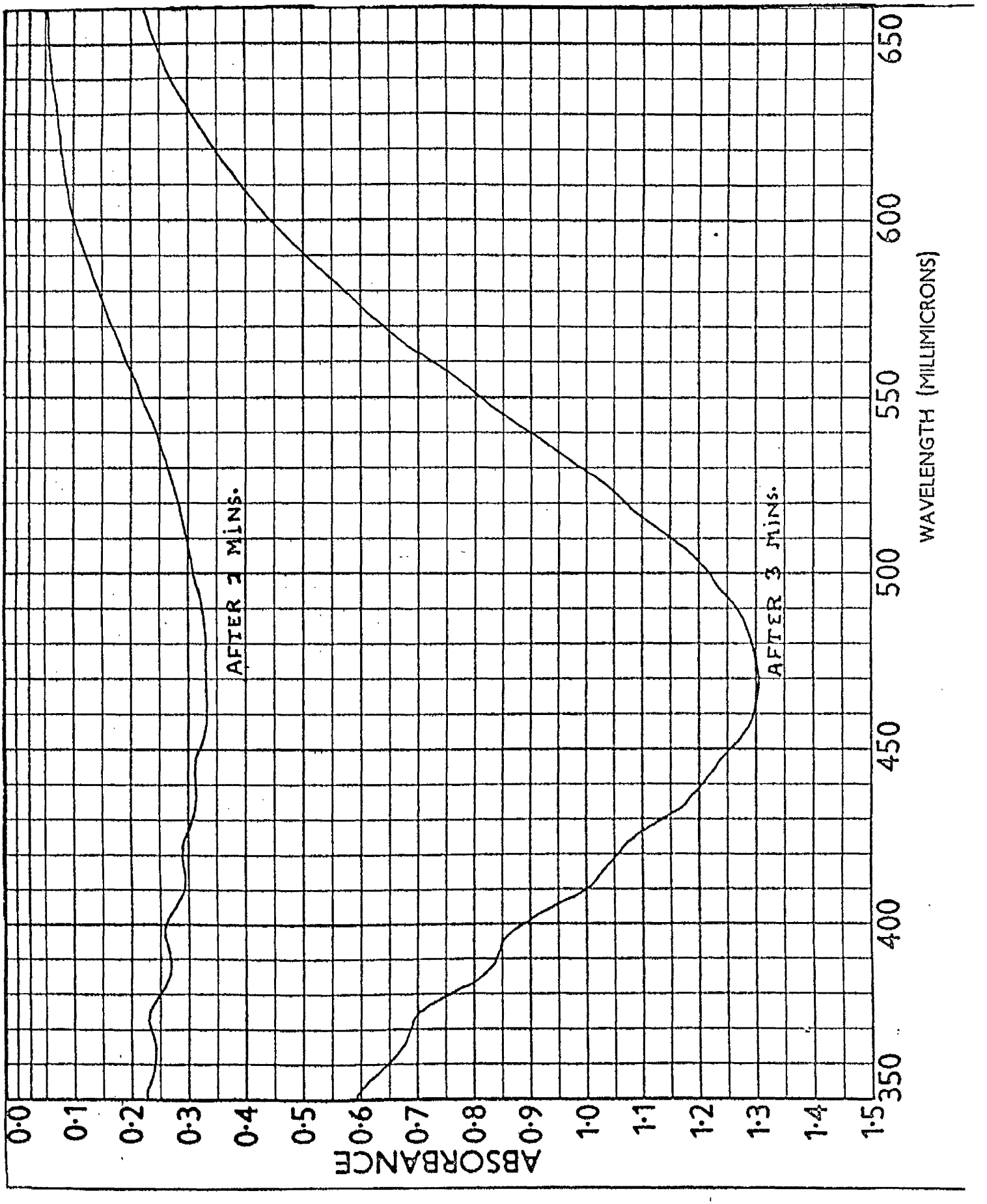
Degradation of PVC fractions. The six fractions obtained by the fractionation of PVC ($F_1$-$F_6$) were subjected to thermal degradation at 198°C in dioctylphthalate. The results are given in Table 16.

Table 16

Degradation of PVC fractions at 198°C in dioctylphthalate

| No. | Intrinsic viscosity dl. gm.$^{-1}$ | concentration gm. l$^{-1}$ | Rate (increase in absorbance minute$^{-1}$) | | | |
|---|---|---|---|---|---|---|
| | | | at 364 mμ | at 386 mμ | at 410 mμ | at 434 mμ |
| 1 | 1.45 | 3.0 | 0.16 | 0.15 | 0.14 | 0.11 |
| 2 | 1.32 | 3.0 | 0.19 | 0.21 | 0.14 | 0.14 |
| 3 | 1.125 | 3.0 | 0.17 | 0.17 | 0.13 | 0.14 |
| 4 | 0.875 | 3.0 | 0.16 | 0.15 | 0.13 | 0.10 |
| 5 | 0.615 | 3.0 | 0.16 | 0.18 | 0.15 | 0.12 |
| 6 | 0.460 | 3.0 | 0.18 | 0.17 | 0.16 | 0.12 |

Fig. 35. Absorption spectra of PVC (Geon-111) degraded in DMF at 178° C



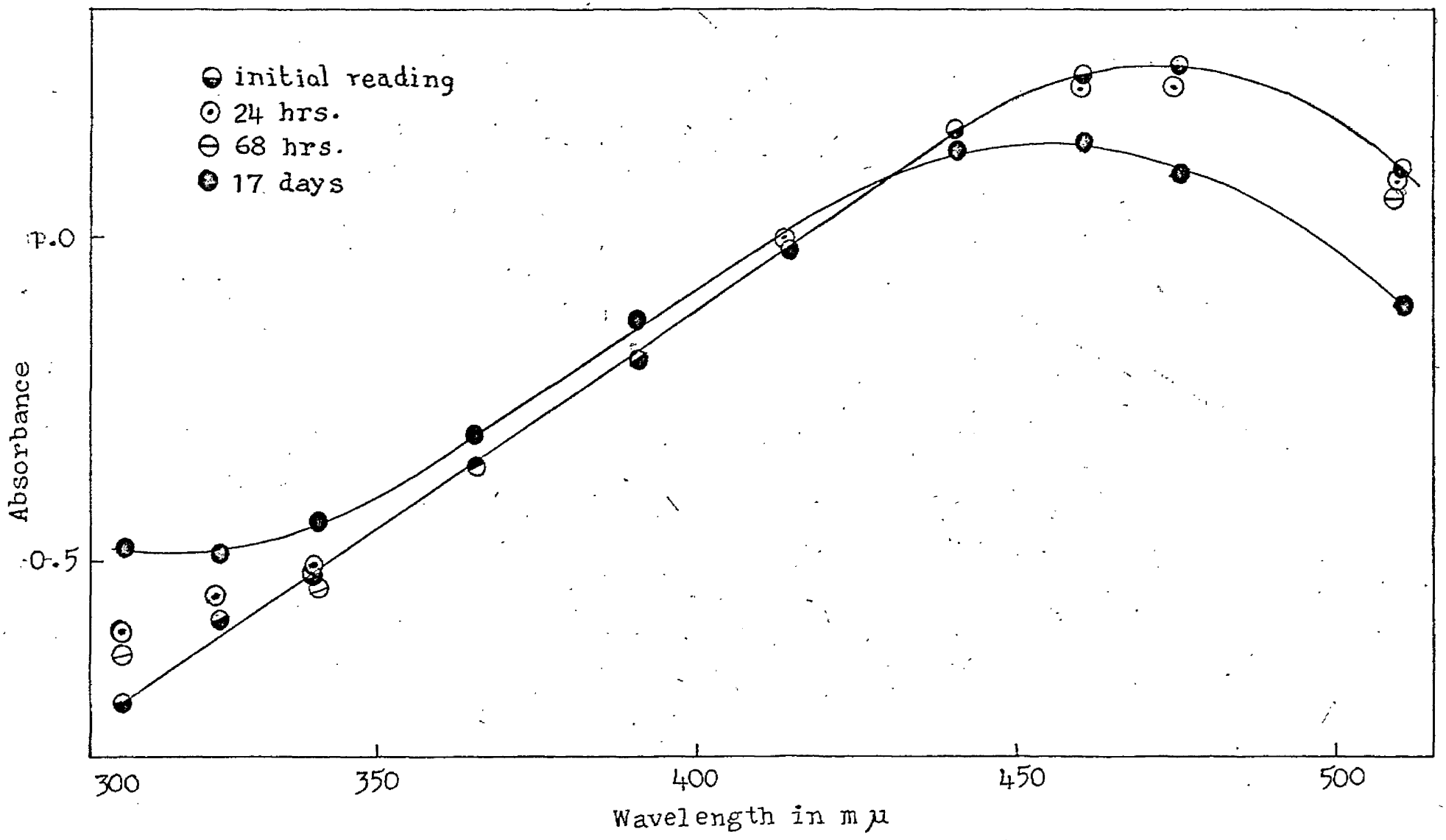
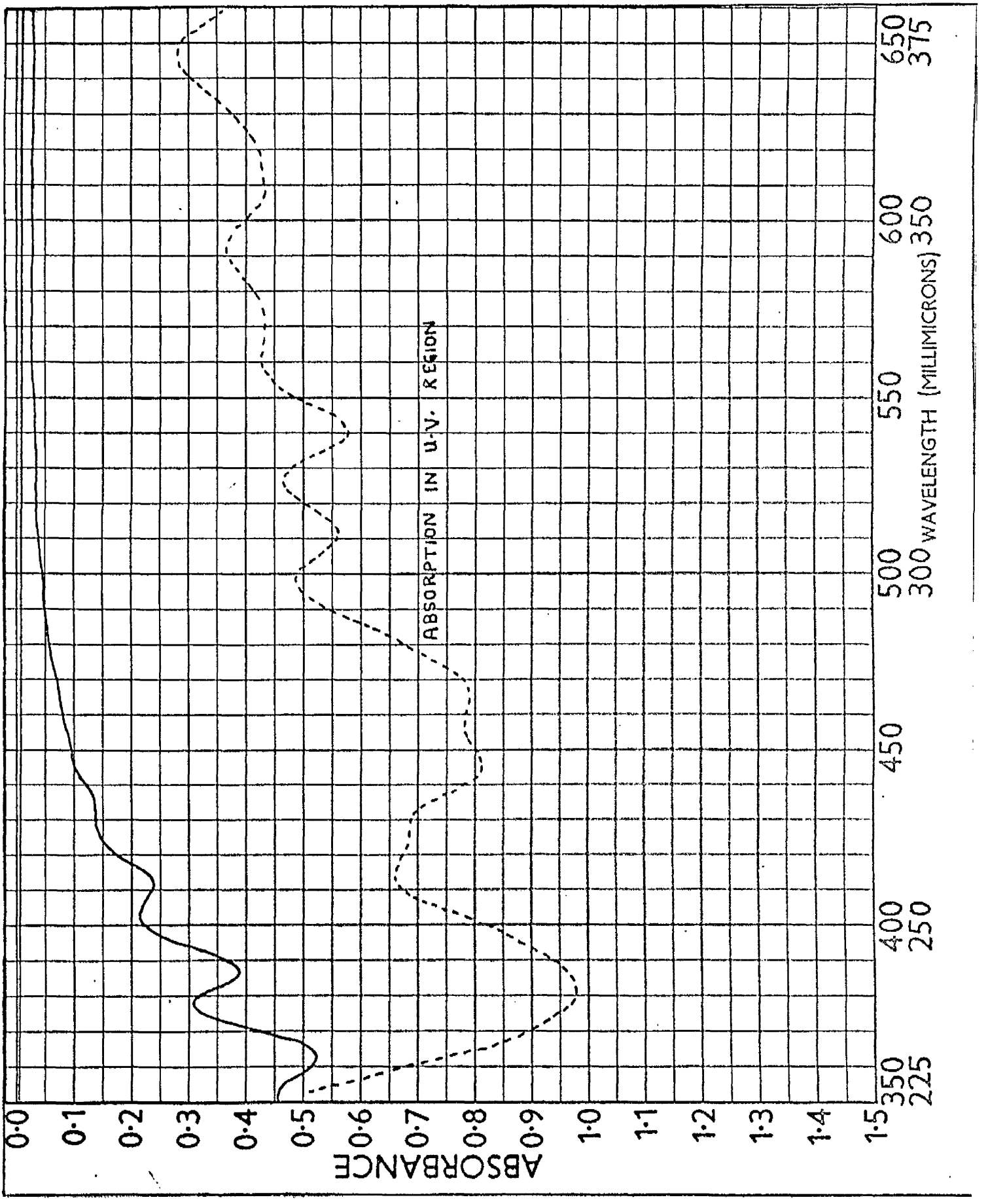



Fig. 36 Effect of storage of degraded PVC solution ( in DMF ) on the absorption spectra

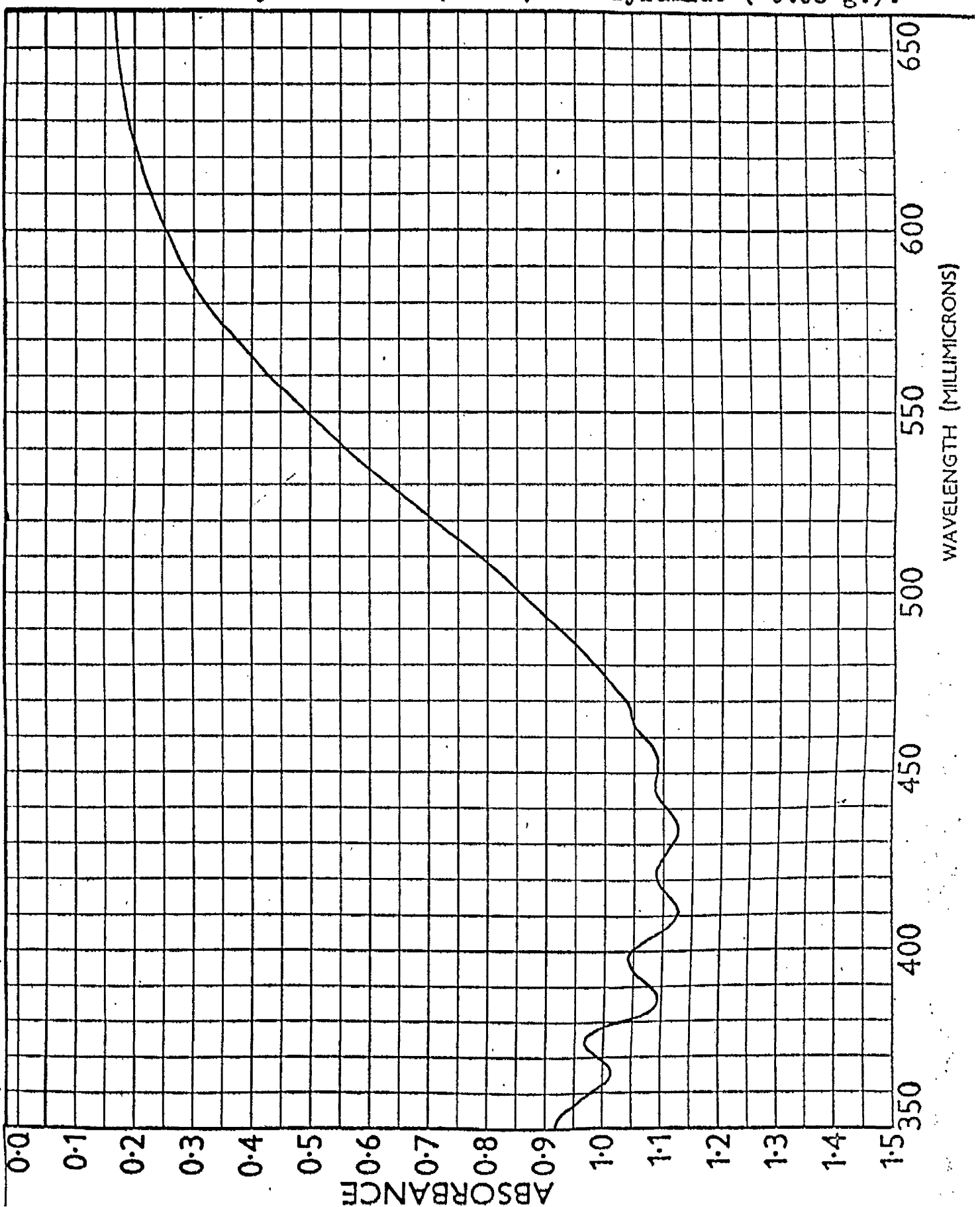
Fig. 37. Absorption spectra of PVC (in tetrahydrofuran ) treated with an alcoholic solution of caustic soda at room temperature under vacuum.



It is evident, there is no systematic increase in rate of colour formation with a decrease in intrinsic viscosity.

Effect of solvents. Some investigations were made using nitrobenzene, dimethyl formamide (DMF) etc. as solvents for PVC. The absorption spectra in nitrobenzene was of similar type as has already been shown for other solvents. However, in DMF an entirely different kind of absorption pattern was observed and the maximum was at 475 m $\mu$ instead of at 364 m $\mu$. The rate of colour production was very fast and in fact at 198°C the solution became black in just three minutes. The distinct peaks observed in other solvents, were not so well defined, and there was a broad absorption band (fig. 35). When this degraded solution was stored at room temperature a decrease in the optical density at higher wavelengths was observed (fig. 36). This different behaviour may be due to the existence of different mechanism for the production of polyene chain. It was believed, that this may be due to the existence of some sort of ionic mechanism of dehydrochlorination. A THF solution of PVC was therefore, degraded by an alcoholic caustic potash solution at room temperature under vacuum. A very systematic formation of double bond compounds was observed. The absorption maximum was at 240 m $\mu$, and the absorption at other wavelengths in order of decreasing optical density was as follows - 274, 286, 321 306, 336, 364, 388, 410, 434, 454 and 474 m $\mu$ (fig. 37). The

Fig 38 Absorption spectra of PVC degraded for 10 minutes at 198°C in presence of ethyl benzoate (2 ml.) & acrylamide ( 0.08 g.).



degradation of PVC in DMF therefore, does not follow the same mechanism as in alcoholic caustic potash.

This different behaviour of PVC in DMF may be due to the presence of an amide group in the solvent. To verify this point, PVC was degraded in ethylbenzoate in presence of acrylamide. The spectra had distinct peaks, but the absorption maxima was at 435 m $\mu$ (fig. 38). Somewhat similar results were obtained when methylene bis acrylamine was used as solvent. In both of these cases, the polymer was precipitated before recording the spectra and slight oxidation of polyene chain may have occured.. It may be said, that the distinct peaks present in acrylamide may be due to the effect of ethylbenzoate, which was used as solvent for PVC. However, degradation of PVC in presence of DMF and ethylbenzoate, gave a spectra typical of DMF.

## Discussion

The absorption spectra obtained in different solvents indicate the presence of polyene chains. Sondheimer[67] has obtained four absorption peaks for polyenes of $H(CH{=}CH)_nH$ type, out of which the two absorption bands at longest wavelength were the most intense. Naylor and Whiting[68] on the other hand have given five absorption bands for polyenes of $CH_3(CH{=}CH)_nCH_3$ type. Our absorption spectra show the existence of several peaks in the visible and ultraviolet region, this may be due

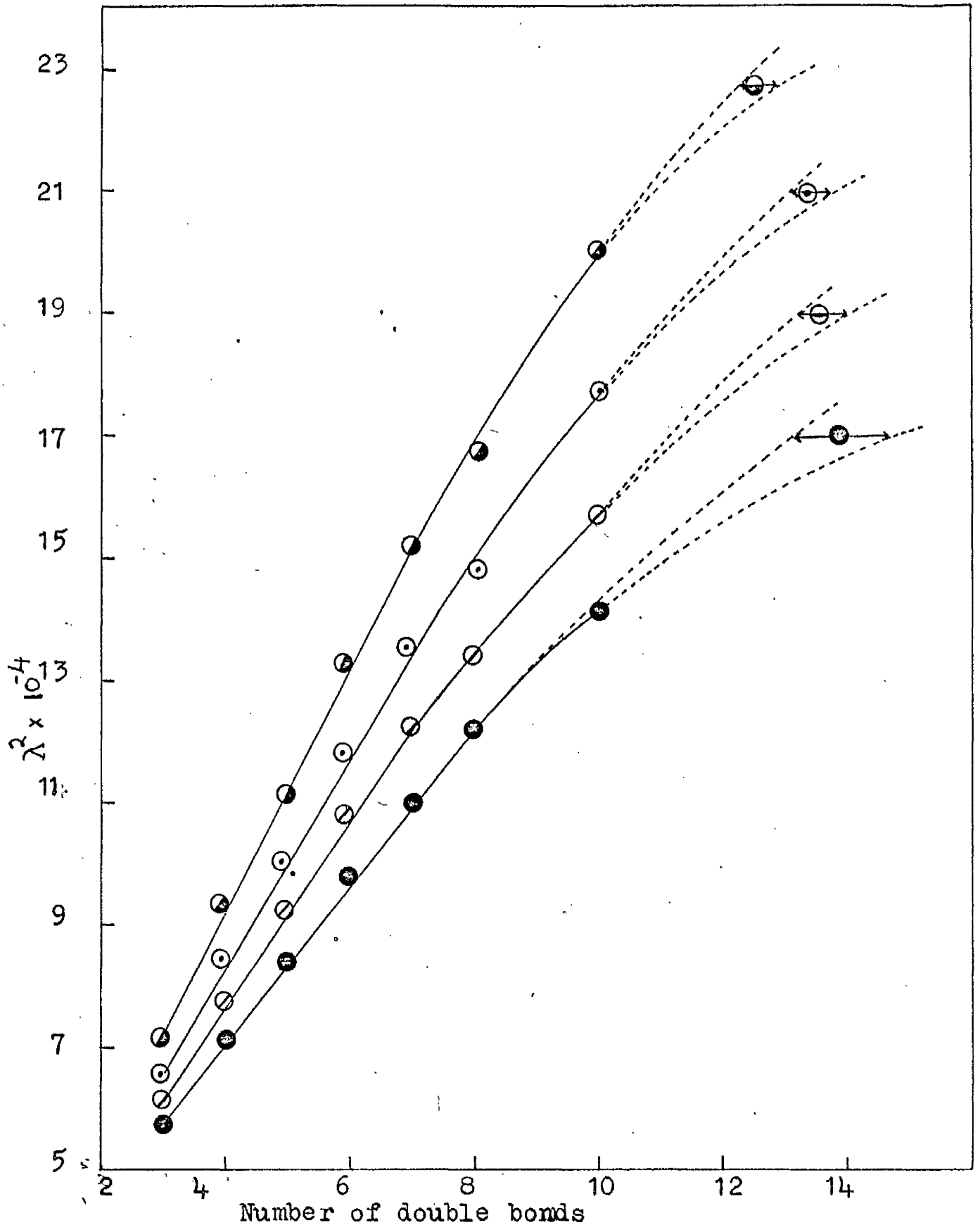



Fig. 39 Relationship between squares of wavelength and number of double bonds of conjugated polyenes.

to the production of polyene chains having different number of double bonds.

The conjugated double bond chain length. Lewis and Calvin[14] have proposed the following relationship existing between wavelength ($\lambda$) and number of double bonds (n)

$$\lambda^2 = kn \quad \text{where k is a constant}$$

They verified this relationship by taking the available data for diphenyl polyenes.

Sondheimer's[67] work on compounds $H(CH=CH)_nH$ with n = 3-10, showed that Lewis Calvin relationship is obeyed fairly well. A plot of n values against the squares of the wavelengths for each of the four longest wavelength maxima produced straight lines as far as n = 7. Small deviations from straight lines occured for the higher compounds. The data of Sondheimer is plotted in fig. 39 and each of the curves are extrapolated for higher n values. The number of double bonds produced in PVC by degradation was estimated by drawing a line at the point of intersection of extrapolated curves with the $^2$ values for the four longest wavelength absorption peaks. Thus a wide range of conjugated double bond chain length is obtained which varied between 12 and 15. However a figure of 13 would satisfy all the points. Atchison[35] obtained a value of n = 16 for PVC subjected to the influence of ionising radiations.

Thus it can be said that when PVC is degraded thermally in different solvents at 198°C, the longest polyene chain produced has approximately 13 double bonds. The banded fine structure peaks at higher temperature (243°C) tend to disappear. These peaks also disappear if polymer is degraded for longer time at 198°C. So some process which reduces the length of the polyene chains, possibly chain scission, must be in operation. Stromberg[20] obtained toluene, benzene and other unsaturated hydrocarbons by degrading PVC at 300°C. These are formed as a result of cyclisation of polyene chain to form benzene ring, with a subsequent scission from the main polymer chain. Perhaps a similar type of mechanism is responsible for disrupting the polyene sequence at 243°C or at lower temperature, if polymer is degraded for more than 30 minutes at 198°C. Druesdow and Gibbs[22] have, however, studied the viscosity changes in nitrogen, but they did not observe any decrease in the initial stages of degradation. But if cyclisation of the polyene chain ends takes place to form benzene, there would be no significant variation in the intrinsic viscosity. Another possibility of the disruption of polyene chain is the addition of some substituent to the double bond. This would cause a disruption of polyene chain by the formation of single bonds.

Polyene chains having more than 13 double bonds are not produced when PVC is degraded in dioctylphthalate, tritoluylphosphate, dichloronaphthalene, benzophenone, ethylbenzoate, benzyl alcohol or nitrobenzene. So a mechanism must be in operation which prevents dehydrochlorination along the polymer chain after some time. Another interesting feature is that the absorption peaks at all above mentioned wavelengths are produced initially, and later on the concentration of these increase. This indicates that dehydrochlorination is fairly rapid to a certain extent along the polymer chain. The stopping of dehydrochlorination after some time may be due to defects in polymer chain, either present initially or produced by dehydrochlorination (as cross-linking).

Though some long chain polyenes are produced (n = 13) a preferential production of polyenes having 4,5 or 6 double bonds take place. The studies using different polymer concentrations indicate that Beer's law is obeyed upto a concentration of 30 $g.l^{-1}$, but after that the concentration of material responsible for absorption does not increase linearly with the polymer concentration. This generalisation, however, applies to systems degraded for 10 minutes at 198°C. In the light of the fact that a cutting down of polyene chains take place at later stages of degradation, one is not justified to conclude

much from this experiment alone. A whole series of experiments, with different polymer concentration, degraded to several time intervals are necessary to draw any significant conclusion. The main drawback of the system we were working with, was that the measurement of absorbance reached its limit after 10 mins. of degradation at higher concentration (30 $g.l^{-1}$) and so the experiments could not be extended beyond that limit. The use of 1 mm. cell instead of 1 cm. cell would perhaps be better for such investigations.

The storage of PVC solution at room temperature caused an increase in the absorption at longer wavelengths. This may be due to the existence of long lived radicals in degraded PVC, which may be responsible for further dehydrochlorination. Similar results have been obtained by subjecting PVC to ionising radiations. Hydrogen and HCl are formed at $-196^{o}C$ on irradiation of PVC and colour develops immediately on warming the solution to room temperature. Several type of radical species are believed to be formed on irradiation of PVC, and it has also been suggested that polymer radicals are formed in pairs at $-196^{o}C$.

$-CH_2CHCl- \longrightarrow -CH_2\dot{C}HCH_2 + Cl\cdot$ (1) Primary radical of pair

$Cl\cdot + -CH_2\dot{C}HCl-$ → $CHCl\dot{C}HCHCl$ (2) unstable

$Cl\cdot + -CH_2\dot{C}HCl-$ → $CH_2\dot{C}ClCH_2$ (3) Secondary radicals of pair

or

$-CH_2CHCl-$ → $CHCl\dot{C}H CHCl + H\cdot$ (2)

$-CH_2CHCl-$ → $CH_2\dot{C}(Cl)CH_2 + H\cdot$ (3) Primary radicals of pair

$H + -CH_2CHCl-$ → $CHCl\dot{C}HCHCl + H_2$

$H + -CH_2CHCl-$ → $CH_2\dot{C}ClCH_2 + H_2$ Secondary radicals of pair

Thus the three polymer radical produced are -

(1) $-CH_2\dot{C}HCH_2$ (2) $CHCl\dot{C}HCHCl$ and (3) $CH_2\dot{C}ClCH_2$

The E.S.R. spectra of PVC at -196°C is of composite nature and perhaps consist of several radical species. The radical (2) is believed to be responsible for propagation of dehydrochlorination and this results in the formation of a radical of fourth type $[-CH=CHCH=CH\dot{C}HCHClCH_2]$. On storage, the E.S.R.

spectra became very narrow indicating a fast disappearance of radicals. Lawton et. al.[37] have suggested that the radical first to disappear is probably $-CH_2\dot{C}HCH_2-$ The existence of three type of radicals has also been suggested by Atchison[34] and Loy[35]. These radicals decay exponentially with time.

$$-CH_2\dot{C}HCH_2 + 2 \text{ or } 3 \longrightarrow -CH_2\underset{|}{\overset{\backslash}{C}}HCH_2- \quad (2 \text{ or } 3)$$

or

$$2 \text{ or } 3 + 3 \text{ or } 2 \longrightarrow 2 \text{ or } 3 \,|\, 3 \text{ or } 2$$

After an initial narrowing of E.S.R. spectra it was observed that further decay was very slow. This has been attributed by Lawton to be due to the existence of a radical stabilised by resonance within a conjugated sequence of double bonds (type 4). The existence of long lived polyenyl radicals of $-CHCl\dot{C}H(CH=CH)_nCHCl$ has also been suggested by Ohinishi et. al.[38] On pyrolysing PVC at 200°C, these authors obtained a very narrow E.S.R. spectrum from which they concluded the existence of polyenyl radicals of long conjugation in thermally degraded PVC.

Thus the storage of a thermally degraded PVC would gradually increase conjugation, as the dehydrochlorination can proceed even

at room temperature. Similar increase in absorption has been observed for irradiated PVC when it is stored at room temperature. There is one difference between thermally degraded PVC and irradiated PVC. Whereas in irradiated PVC the storage resulted in shifting of absorption maxima to higher wavelengths, the storage of thermally degraded PVC solution at ambient temperature only caused the increase in concentration of polyene chains.

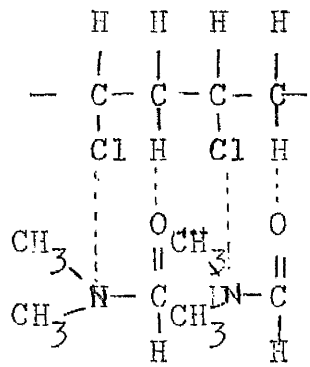
Morokuma[38] has calculated electronic absorption bands of polyenyl radicals of various lengths - (244 - 250) m $\mu$ = 1, (290 - 291) m $\mu$ = 2, (330 - 332) m $\mu$ = 3, (368 - 373) m $\mu$ = 4, (400 - 404) m $\mu$ = 5, (430 - 435) m $\mu$ = 6, (460 - 462) m $\mu$ = 7, (485 - 487) m $\mu$ = 8, 510 m $\mu$ = 9. Thus a polyenyl radical of 8 conjugated double bonds would correspond to 485 m $\mu$, the $\lambda_{max.}$ for absorption of thermally degraded solution of PVC.

Another explanation for the production of a polyene chain with a limited number of double bonds could perhaps be given by the stability of the polyenyl radical. It may be possible that, the resonance stability of the polyenyl radical is increased to an optimum upto a certain length of conjugated double bonds, and after that there is no or little change in its stability. This may well be due to the change in the planarity of molecule.

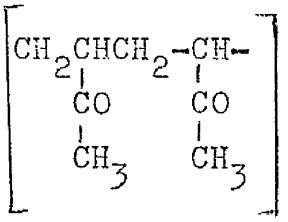
An increase in the optical density at longer wavelengths was observed when polymer was degraded for 460 minutes in ethyl-benzoate. This may happen if the energy barrier which stops dehydrochlorination is overcome by prolonged heating. Guyot et. al.[21] have suggested that thermal dehydrochlorination at 180°C proceeds to some extent and is then stopped. This results in the formation of conjugated double bonds, and part of macro-molecular chain is left intact, which may produce a new chain of reactions in conditions which are suitably active. They have based this argument on the dehydrochlorination studies of PVC in the temperature range 150 - 190° and 200 - 250°C. One of the objections that can be raised against this argument is that such an energy barrier would be easily overcome at higher temperatures. If this is the case, it is difficult to under-stand why we have observed a decrease in the optical density at longer wavelengths. Perhaps the answer could be that chain scission of polyene chains and dehydrochlorination are two competing reactions at higher temperatures. Thus the production of fewer long chained polyenes does not necessarily mean less dehydrochlorination. This is supported by the fact that HCl continues to be evolved at a high rate after absorption stops increasing rapidly.

The disappearance of colour when solution is exposed to atmosphere is probably due to the oxidation of double bonds, which would lead to the formation of peroxy and oxy radicals, and finally to ketonic compounds. This is known to happen in polyene systems.

It is a bit difficult to explain the entirely different absorption spectrum obtained in dimethyl formamide. The possible explanation may be that the DMF molecule takes an active part in dehydrochlorination by forming weak links with the hydrogen and chlorine atoms of the polymer chain.



This type of hydrogen bonding between H atom attached to carbon and ketonic groups is open to criticism because hydrogen bond formation generally take place between a hydrogen atom attached to O, N or F[69]. Though the existence of a hydrogen bond between an electron donor and a hydrogen atom attached to a carbon atom has not been definitely proved, but its possibility

can not be denied. Thus the greater solubility of organic compounds containing donor centres (as polymethylvinylketone)  in chloroform as compared to carbon tetrachloride has been explained[70] by the formation of $-CH\leftarrow O$ type of hydrogen bonds.

Thus the formation of links between oxygen and hydrogen and nitrogen and chlorine, weakens the C-Cl and C-H bonds which consequently breaks down at higher temperature involved in thermal degradation. This leads to the formation of HCl and a double bond. Since the reaction was carried in presence of excess of solvent (polymer concentration = 17 $g.l^{-1}$) the interaction between DMF molecule and polymer molecule would be very marked and a long conjugated polyene structure would be introduced easily. This mechanism also explain that the branching of $\sim CH=\overset{|}{C}-CH_2\overset{|}{C}HCl-$ this type would not affect dehydrochlorination in presence of DMF, but these might represent a polymer chain end in a radical mechanism. Branch points of $\sim CH_2CHClCH_2\overset{|}{C}H-CH_2CHCl\sim$ type would affect the dehydrochlorination by both the mechanism. The occassional presence of head to head and tail to tail structures would affect the dehydrochlorination by radical mechanism ($-CH_2CHClCHClCH_2CH=CH-CH=CH-$) but it would be independent of this termination in presence of dimethyl formamide.

At this stage it would be worthwhile mentioning the results of Wippler[70] who studied affect of ionising radiations on PVC in presence of DMF. He obtained 97% gel formation by this reaction. Wippler has not given any explanation for the high yield of gel.

Table 17

Solubility of irradiated PVC in THF as a function of swelling agent

| Swelling agent | PVC insoluble % | Swelling agent | PVC insoluble % |
|---|---|---|---|
| THF | 90 | acetone | 5 - 8 |
| Cyclohexanone | 0 | benzene | 44 |
| Dioxane | 80 | tetralin | 40 |
| Butanone | 5 - 10 | DMF | 97 |
| Ethylene oxide | 90 | acetone benzene 60/40 | 40 |

in presence of DMF, but perhaps it could also be explained by the reaction proposed by us. The ionisation studies are usually carried out at fairly low temperatures, and this would limit the motion of polymer chains. This may, increase the possibility of a bridge formation between two polymer chains. This reaction would be facilitated by DMF.

Our experiments with 6 PVC fractions show no appreciable difference, as far as the production of polyene chains is

concerned. This is in contrast to the findings of previous workers. Talamini and Pezzin[12] have recently published a paper in which they have reported that rate of dehydrochlorination is independent of molecular weight. They prepared the different molecular weight polymers by fractionation of polyvinyl-chloride. Similar results on dehydrochlorination have also been obtained by Distiller's Company (Private talks). On the basis of absorption studies and dehydrochlorination work (Chapter 3) we can conclude that rate of polyene chain formation is not inversely proportional to the degree of polymerisation. The commercial polymer is prepared by taking the conversion roughly upto 90%. This would introduce more branching in the high molecular weight species. Perhaps these branches also act as initiators of dehydrochlorination. It may be said that branches also have end groups and thus the number of end groups would be increased due to presence of branching in the high molecular weight species.

Suppose the mean molecular weight of linear polymer is n.

Let the number of branches = $\ell$

Here we are assuming that branches can grow to the same extent as the main polymer chain.

The molecular weight of such a polymer would then be equal to $n(\ell+1)$

The number of end groups would be $l+2$

$$\text{Then } \frac{\text{molecular weight}}{\text{no. of end groups}} = \frac{(l+1)n}{l+2}$$

In the linear polymer where $l=0$, a value of $\frac{n}{2}$ would be obtained i.e. there would be two end groups per polymer chain.

On the other hand if $l=4$ then -

$\frac{(4+1)}{4+2} = \frac{5n}{6}$ i.e. there would be 6 end groups for a polymer of 5 times high molecular weight than a linear polymer.

This above discussion clearly indicates that number of end groups would be much more in case of low molecular weight material than high molecular weight branched material. Branched polymers may have tertiary chloride which may also increase instability of polymer. A kind of compensating action between more branches and less end groups (for high molecular weight polymer) and more end groups and less branches (low molecular weight polymer) may be imagined to exist. The unpublished work of Bengough and Onozuka[72] indicates that total sum of end groups and branches for low and high molecular weight PVC is approximately the same .

On this basis perhaps it would be easy to explain the results of Bengough and Sharpe[9], who observed an inverse relationship between rate of dehydrochlorination and degree of polymerisation. These workers prepared PVC of different

molecular weight by carrying the polymerisation at different temperatures, and upto a low conversion (10%). Branches are usually formed at high conversion. Thus the high molecular weight material which they were dealing with must have been more linear than the corresponding fraction of commercial polymer. In a linear polymer chain ends would be the determining factor for the dehydrochlorination.

# CHAPTER 4

## Section B

### Degradation of PVC in presence of monomers

Winkler[17] suggested the existence of free chlorine atoms in the mechanism of PVC dehydrochlorination. If this is correct, then there is no reason why the free chlorine atom (or any other free radical) should not initiate the polymerisation of any monomer. The removal of chain carriers (as chlorine atoms) should retard the dehydrochlorination and consequently PVC would be stabilised in presence of monomers. It was with this aim, that the effect of monomers on PVC degradation was investigated.

### Experimental

The monomers selected were -

styrene, α-methyl styrene, o-chlorostyrene, vinyl benzoate, 1.1 diphenylethylene, n-butylmethacrylate, methacrylic acid, acrylic acid, acrylamide, methylene bis acrylamine, hydroxyl-methacrylate, butane 1.4 dioldimethacrylate and triethylene glycol diacrylate.

The monomers acrylamide, methylene bis acrylamine acrylic acid etc. were used as such without any purification but the rest were distilled under reduced pressure.

The degradation of polymer was carried out in sealed tubes.

Weighed quantities of polymer were placed in small tubes each having a constriction for sealing off. The monomer

was then added by a narrow capillary. In those cases where a solvent was used, it was added prior to the addition of the monomer. The tubes were evacuated and degassed on a vacuum line and then sealed off at the constriction. These tubes were heated in a vapour jacket at 198°C for various times and the colour changes were noted.

It is quite evident from the given table that styrene and α-methyl styrene are the best inhibitors of colour formation among the monomers that were studied here. The polymer discoloured in all the remaining substances to a lesser or greater extent. In some monomers gelation was fairly rapid (triethylene glycol diacrylate, n-butyl methacrylate, hydroxymethyl acrylate and butane 1.4 dioldimethacrylate) and either a very viscous solution or a solid was obtained after the treatment.

Table 18

Effect of monomers on PVC discolouration at 198°C

| No. | Name of substance added | weight of polymer gms. | Amount of substance added | Solvent | heating time mins. | Colour |
|---|---|---|---|---|---|---|
| 1 | Styrene | 0.0980 | 2 ml. | 2 ml. | 60 | no colour |
| 2 | " | 0.0790 | 0.2 ml. | 2 ml. | 60 | yellow |
| 3 | " | 0.0750 | 1 ml. | x | 60 | yellow tinge |
| 4 | α-methyl styrene | 0.0880 | 2 ml. | 2 ml. | 60 | no colour |
| 5 | " " | 0.0980 | 1 ml. | 2 ml. | 60 | yellow tinge |
| 6 | " " | 0.1280 | 0.3 ml. | 2 ml. | 60 | " " |
| 7 | " " | 0.048 | 2 ml. | x | 60 | no colour |
| 8 | O-chloro styrene | 0.1084 | 1 ml. | 2 ml. | 60 | yellow |
| 9 | " " | 0.1074 | 2 ml. | x | 60 | brown |
| 10 | Vinyl benzoate | 0.1104 | 2 ml. | 2 ml. | 60 | yellow |
| 11 | " " | 0.1104 | 2 ml. | x | 60 | yellow |
| 12 | n-butylmethacrylate | 0.082 | 2 ml. | 2 ml. | 60 | yellow |
| 13 | " | 0.0752 | 2 ml. | x | 60 | yellow tinge |
| 14 | Acrylic acid | 0.1206 | 2 ml. | 2 ml. | 60 | brown |
| 15 | " " | 0.1304 | 2 ml. | x | 60 | brown |
| 16 | Acrylamide | 0.1140 | 0.1160 g. | x | 12 | brown |
| 17 | " | 0.1094 | 0.084 | 2 ml. | 10 | red |
| 18 | Methylene bis acrylamine | 0.1160 | 0.080 g. | 2 ml. | 10 | orange |

Table 18 (cont.)

Effect of monomers on PVC discolouration at 198°C

| No. | Name of substance added | Weight of polymer gms. | Amount of substance added | Solvent | heating time mins. | Colour |
|---|---|---|---|---|---|---|
| 19 | Methylene bis acrylamine | 0.113 | 0.098 g. | x | 5 | brown |
| 20 | Hydroxymethyl acrylate | 0.108 | 2 ml. | 2 ml. | 5 | yellow |
| 21 | butane 1,4-dioldimeth-acrylate | 0.108 | 2 ml. | 2 ml. | 30 | yellow |
| 22 | butane 1,4-dioldimeth-acrylate | 0.111 | 2 ml. | x | 30 | yellow |
| 23 | triethylene glycol-diacrylate | 0.054 | 1 ml. | 1 ml. | 30 | orange |
| 24 | 1,1-diphenylethylene | 0.139 | 2 ml. | x | 60 | brown |
| 25 | " | 0.135 | 2 ml. | 2 ml. | 60 | brown |

A few experiments were then performed to investigate the amount of polystyrene produced in the presence and absence of PVC at 198°C. A weighed quantity of polymer was dissolved in ethylbenzoate and 2 ml. of styrene were added. The solution was evacuated off and degassed in the usual manner and degraded for 1 hr. at 198°C. It was then dissolved in tetrahydrofuran and acetone and precipitated by methanol. The precipitated polymer was filtered, dried and weighed in a sintered glass crucible.

Weight of precipitate (PVC + polystyrene) = 1.2814 gm.

$\therefore$ wt. of polystyrene = 1.1830 gm.

A blank of styrene and ethylbenzoate under similar conditions gave 1.2198 gms. of polystyrene.

The experiment was repeated again, to verify the results. Again it was observed that amount of polystyrene produced in blank was greater than in presence of PVC. However, the difference in weight this time was 0.059 gm. instead of 0.036 gm. as reported by first experiment.

A similar experiment in presence of PVC and ethylbenzoate was performed with vinylbenzoate. The weight of polyvinylbenzoate produced in blank was 0.0310 gm. and in presence of PVC it was 0.0340 gm.

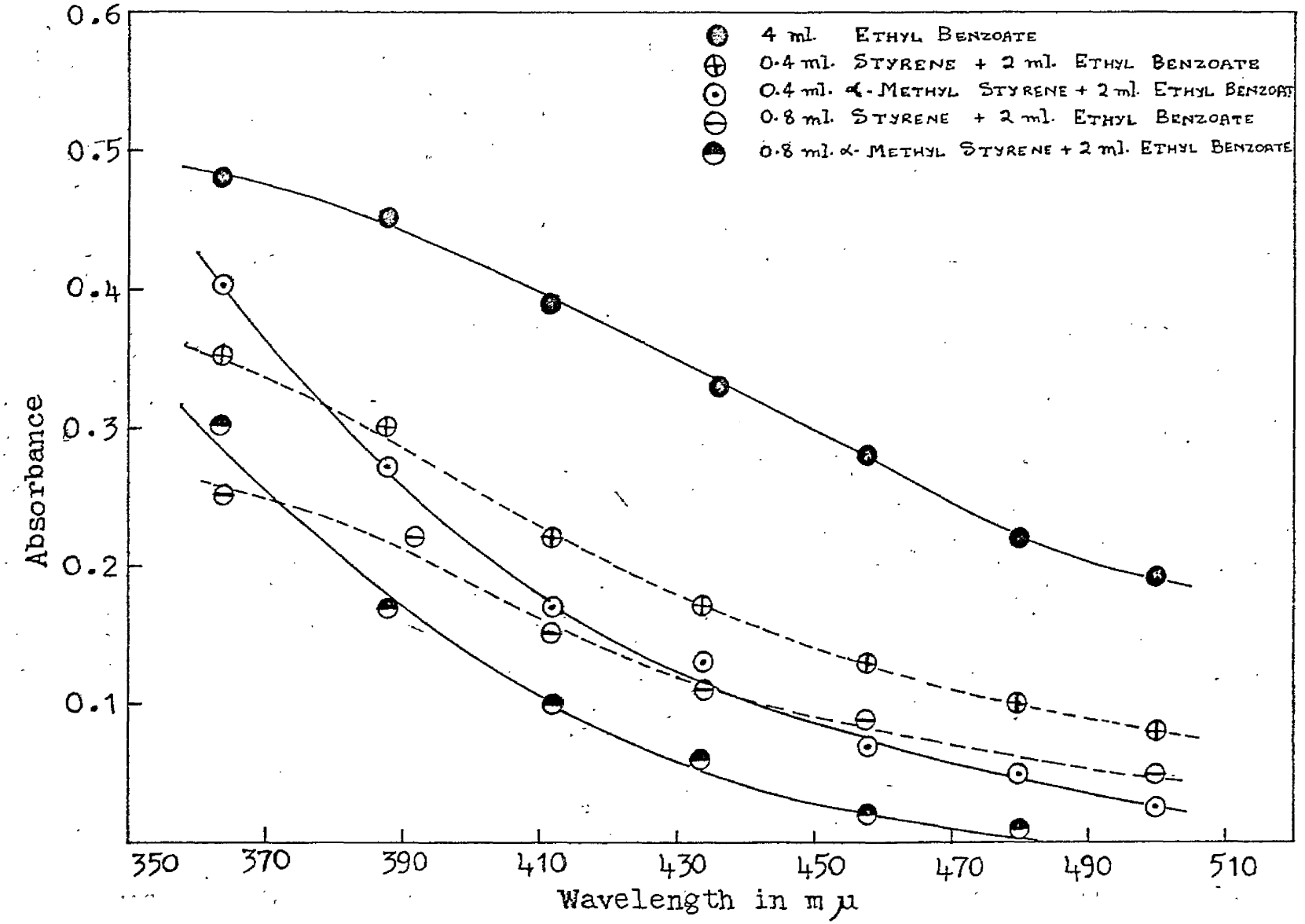
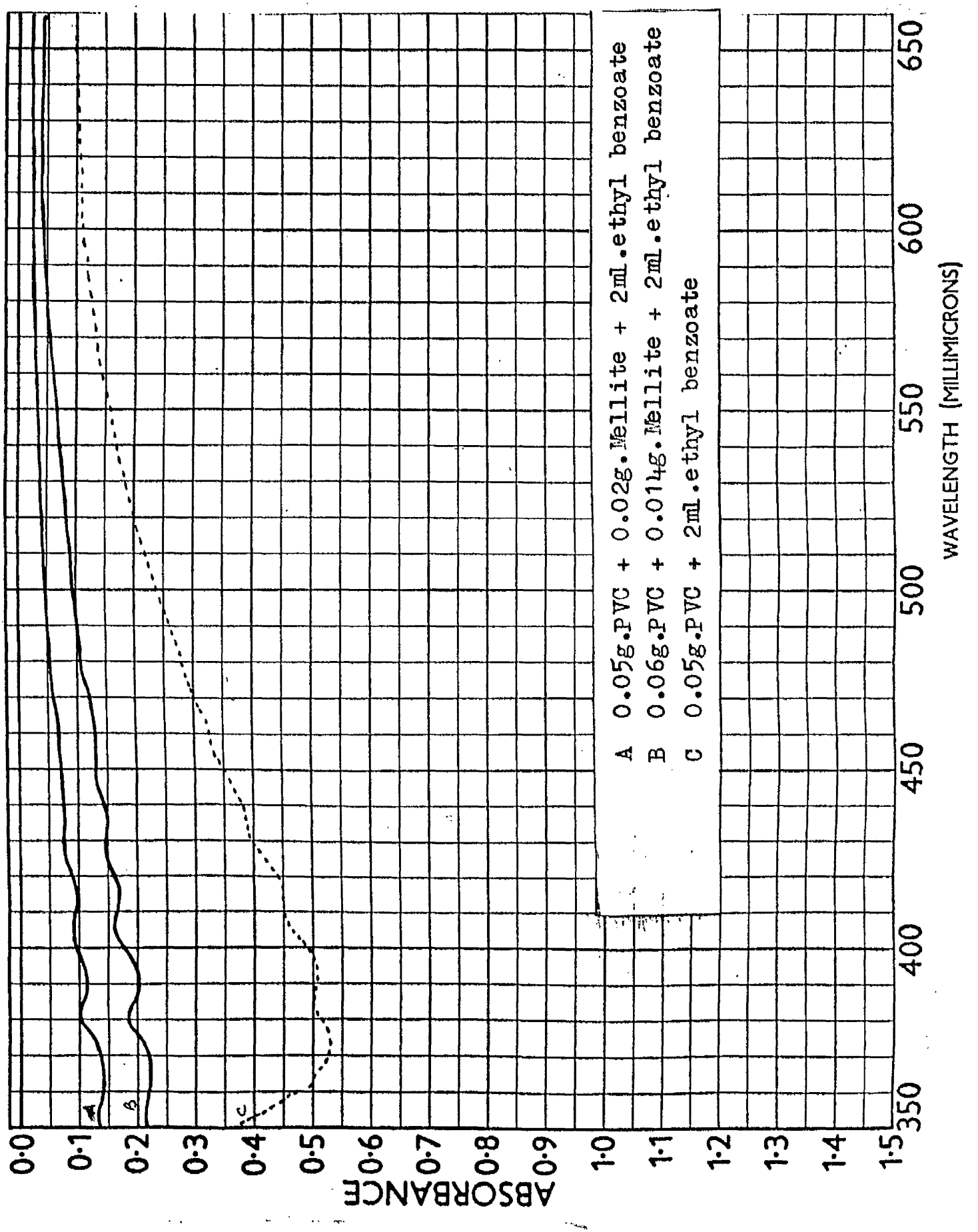



Fig. 4Q Absorption spectra of PVC ( precipitated ) in presence of monomers ( Styrene and α methyl styrene ).

Fig.41. Absorption spectra of PVC degraded for 1 hour at 198° C in presence of Mellite and ethyl benzoate.



Another experiment was then performed to investigate the influence of styrene on degraded PVC. A PVC solution degraded in ethylbenzoate (yellow colour) was added to 2 ml. of styrene, evacuated, sealed off and heated at 198°C. The solution became colourless.

It was then decided to follow the colour changes in presence of styrene and α-methyl styrene by ultraviolet spectrophotometer. It was observed that fewer long chain polyenes are produced even in the presence of 0.4 ml. of α-methyl styrene. The results of this degradation are shown in fig. 40.

The effect of commercial stabilisers as Flamex, Stanclere 8C and Mellite was also investigated. The polymer was discoloured to some extent in all the stabilisers. The absorption spectra obtained in presence of Mellite is given in fig. 41.

## Discussion

Styrene and vinylbenzoate are at two extremes of monomer reactivity. Styrene is a very reactive monomer, whereas vinylbenzoate is not. The basic idea in selecting these two monomers was to distinguish between the radicals of

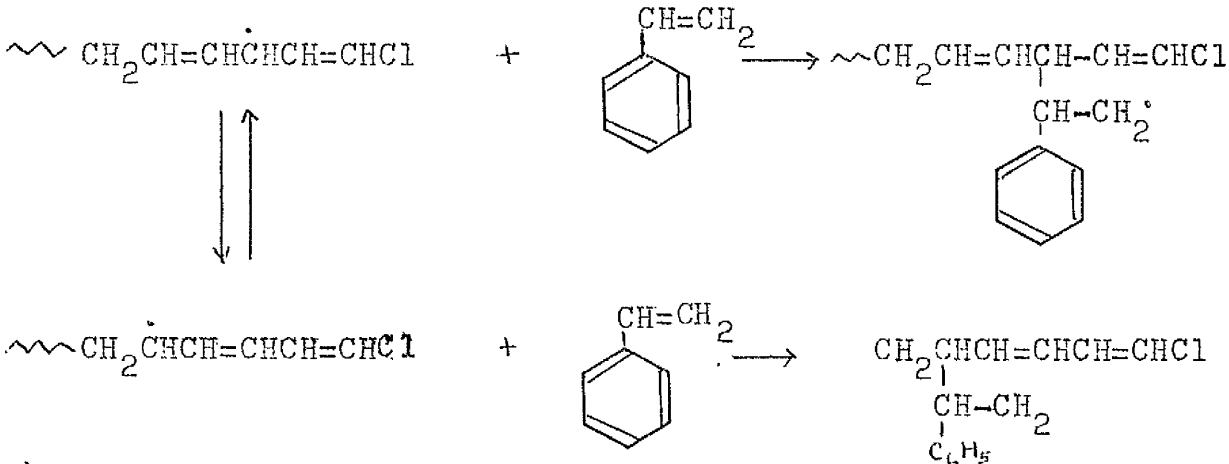
(1) $\sim\sim\dot{C}HCH{=}CH\sim\sim$ and (2) $\dot{C}l$ types.

Styrene, being a reactive monomer would react with both (1) and (2) whereas vinylbenzoate would only react with (2). This is because (1) is a resonance stabilised radical while (2)

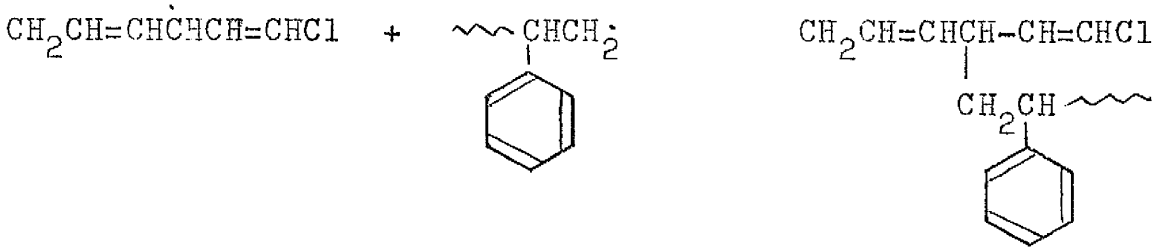
is a very reactive chlorine atom. If both (1) and (2) radicals were involved in the degradation of PVC then the discolouration of PVC should be retarded in presence of both styrene and vinylbenzoate, which is not the case. The addition of vinylbenzoate to PVC solution in ethylbenzoate did not alter the absorption spectra, whereas in styrene the colour formation was inhibited. These results indicate that radicals of low reactivity ((1)) are involved in the thermal degradation of PVC.

The inhibiting action of styrene can be explained by a reaction with PVC radical. There are two possible ways to such reaction.

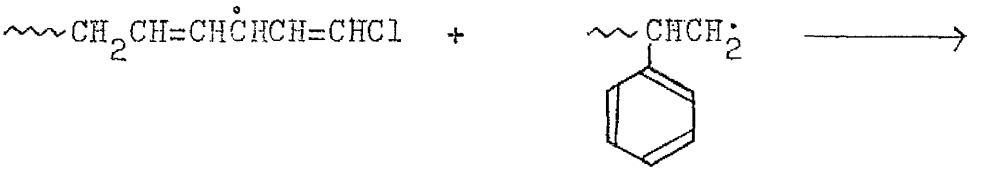
(a) addition of styrene to the radical which would initiate the polymerisation of styrene

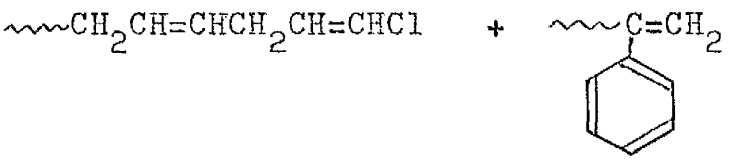


(b) termination of PVC radical and styryl radical (produced under the influence of heat) by a combination reaction



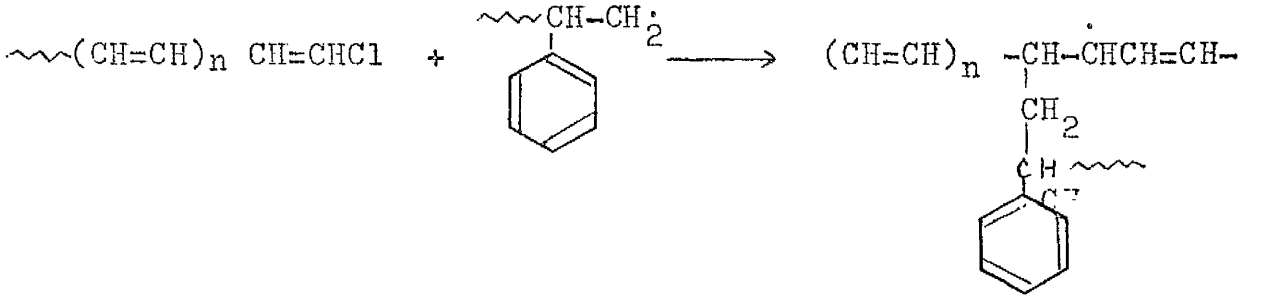
or by disproportionation





One would expect to get an increase in polymer formation in presence of (1) and (2) radicals. This is, however, not the case. This also support the absence of reactive atoms like chlorine. The concentration of radicals of (1) type may not be very high and perhaps this is one of the reasons for the insignificant increase in polyvinyl benzoate formation. Another possibility may be that reaction (a) and (b) are competing reactions and thus whatever initiation may have taken place, the chain is soon terminated. The formation of comparativly less polystyrene in presence of PVC than its absence also indicates that some type of chain reactions are taking place.

The above scheme thus explains that styrene acts as an inhibitor for colour formation by disrupting the free radical chain of degrading PVC. This scheme, however, does not account for the effect of styrene on PVC subjected to previous degradation. This may be explained if the styryl radicals react with conjugated polyene chain.



or by a kind of Diels' Alder reaction.

# CHAPTER 5

## Light scattering measurements of (a) polyvinylchloride (b) thermally degraded polyvinylchloride in cyclohexanone

Staudinger proposed the first relationship between solution viscosity and molecular weight which was later modified by Mark[73] and Houwink[74] to its present form -

$$[\eta] = K M^{a} \qquad (6)$$

where $[\eta]$ = intrinsic viscosity or limiting viscosity number

$K$ = constant

$M$ = molecular weight (viscosity average)

The value of 'a' depends upon the shape of the polymer molecule and also on its interaction with solvent.

If $c_i$, $m_i$ and $M_i$ are the weight concentration $gl.^{-1}$, molar concentration and molecular weight of the ith species respectively then the various molecular weight averages for the polymer solution could be defined as follows -

Z - average molecular weight

$$\bar{M}_Z = \frac{\sum c_i M_i^2}{\sum c_i M_i} = \frac{\sum m_i M_i^3}{\sum m_i M_i^2} \qquad (7)$$

Weight average molecular weight

$$\bar{M}_w = \frac{\sum c_i M_i}{\sum c_i} = \frac{\sum m_i M_i^2}{\sum m_i M_i} \qquad (8)$$

Number average molecular weight

$$\bar{M}_n = \frac{\sum c_i}{\sum c_i M_i} = \frac{\sum m_i M_i}{\sum m_i} \qquad (9)$$

Several research workers[75-78] have studied the viscosity molecular weight relationship of PVC in different solvents. However, most of these correlations were made between viscosity and number average molecular weight. The property used for determining the number average molecular weight (e.g. osmotic pressure) depends entirely on the number of molecules and is independent of their size, while the property used for evaluating viscosity average and weight average molecular weight depend both on number and size. Thus the latter two averages lie closer to each other than does the number average molecular weight.

The more closely the values for $\bar{M}_n$ and $\bar{M}_w$ approach each other, the narrower is the molecular weight distribution. In those cases where $\bar{M}_w$ is equal to $\bar{M}_n$ the polymer is monodisperse.

In table 19 the values of 'K' and 'a' determined by various workers are given (the intrinsic viscosity is expressed as dl. gm.$^{-1}$)

Table 19

Relation between $[\eta]$ in cyclohexanone and the molecular weight of polyvinylchloride

| No. | Authors | Solvent | K | a | Temperature °C | Mol. wt. | Comments |
|---|---|---|---|---|---|---|---|
| 1 | Hengstenberg[75] | cyclohexanone | $1.95 \times 10^{-4}$ | 0.79 | 25 | $\bar{M}n$ | unfractionated |
| 2 | Breitenbach[76] | cyclohexanone | $1.16 \times 10^{-4}$ | 0.85 | 20 | $\bar{M}n$ | " |
| 3 | Mencik[77] | cyclohexanone | $2.04 \times 10^{-3}$ | 0.56 | 25 | $\bar{M}n$ | fractions |
| 4 | Danusso[78] | cyclohexanone | $2.4 \times 10^{-4}$ | 0.77 | 25 | $\bar{M}n$ | unfractionated |
| 5 | Bier and Krämmer[51] | cyclohexanone | $1.13 \times 10^{-3}$ | 0.63 | 25 | $\bar{M}n$ | fractionated |
| 6 | Mead and Nuoss[54] | cyclohexanone | $1.13 \times 10^{-5}$ | 1 | 25 | $\bar{M}w$ | fractionated |
| 7 | Ciampa and Schwindt[79] | cyclohexanone | $1.10 \times 10^{-5}$ | 1 | 25 | $\bar{M}w$ | unfractionated |
| 8 | Freeman and Manning[80] | THF | $1.63 \times 10^{-4}$ | 0.766 | 25 | $\bar{M}w$ | fractionated |
| 9 | Moore and Hutchison[81] | cyclohexanone | $2.08 \times 10^{-3}$ | 0.56 | 25 | $\bar{M}n$ | " |
| 10 | " " " | | $1.74 \times 10^{-3}$ | 0.55 | 25 | $\bar{M}w$ | " |
| 11 | Kobayashi[52] | THF | $2.19 \times 10^{-1}$ | 0.54 | | $\bar{M}w$ | " |

Papers on light scattering measurements of polymer solutions usually contain some extrapolation diagrams. But in the case of PVC we have found only one paper by Kratochvil[82] which has given extrapolation diagrams. Doty and coworkers[45] were the first to use the light scattering (dissymmetry) method for evaluating the molecular weight of PVC in dioxane. Ciampa and Schwindt[79] measured $\bar{M}_w$ of unfractionated sample dissolved in cyclohexanone but have not given the experimental and evaluation procedure. Similarly Gautron and Wippler[83] have not mentioned the evaluation procedures. Baker[84] used tetrahydrofuran as the solvent and used the dissymmetry method for calculation. Kobayashi[52] has mentioned a Zimm plot but showed the measurements only at three lower angles. All this indicates some sort of anomaly in the literature. We, therefore, decided to study the molecular weight of PVC (Geon III) by light scattering technique. Four of the PVC fractions ($F_2$,$F_4$,$F_5$,$F_6$) were also studied. We could not extend our studies to all the fractions, partly because of the small quantity of fractions, and partly due to the use in dehydrochlorination and absorption studies.

Other informations, such as molecular dimensions, second virial coefficient and number average molecular weight could also be obtained from such a study.

Association of PVC

The presence of aggregates of PVC molecules in solution was indicated by Doty and coworkers[45]. Two peaks were observed in the ultracentrifuge experiments, and a decrease in apparent molecular weight was found when a solution of PVC was heated from 25° to 64°C. Gautron and Wippler[83] investigated the association of PVC in tetrahydrofuran and they concluded that heating for 15 minutes at 110°C is sufficient to break the association. Other workers[85,86] have also studied this association of PVC. Hengstenberg[86] believes that the formation of 'microgel' is influenced by the solvent, the solution process, and the molecular weight of the polymer.

The presence of these aggregates complicates the molecular weight determination by light scattering. The scatter at lower angles is tremendously increased due to this microgel, and consequently a very high apparent value for the weight average molecular weight is obtained. The influence of microgel on solution viscosity is not so marked[83,86]. Heating of the solutions prior to light scattering measurements is, therefore, necessary. Some of these microgels are, however, fairly stable to temperature[82].

In fact the existence of microgel stable upto 100°C was found in two fractions of PVC ($b_1$ and $b_2$) in this work.

Degradation of PVC

The degradation of PVC has received considerable study, but little information is available regarding the changes in the

structure of the polymer during degradation. Viscosity measurements on degraded polymer have been made by Baum and Wartman[11]. These workers observed a slight increase in intrinsic viscosity when PVC was heated at 170°C for four hrs. (value of $[\eta]$ changed from 1.10 dl.gm.$^{-1}$ to 1.20 dl.gm.$^{-1}$)

Light scattering, as it is an absolute method of determining molecular weights, might give a clearer picture of such changes in the polymer. It was with this aim that the degradation was followed using light scattering technique.

Ultracentrifuge measurements

The association of PVC in solution has been investigated by some workers[45,83,86] using ultracentrifugal analysis. The velocity of sedimentation of macromolecules in solution under the influence of a centrifugal field could be determined by this method. Under the influence of a high centrifugal field, the solute molecules which are initially uniformly distributed throughout the solution settle at appreciable rate towards the outer surface of the cell. Inbetween the two regions thus formed (i.e. a region of no solute and another of uniform concentration or plateau region) is the transition zone where concentration varies with distance from the axis of rotation. The movement of this transition zone or boundary can be followed optically by means of a Schlieren device. The associated

molecules of PVC which would be of very high apparent molecular weight would sediment much faster than the unassociated molecules. Thus the appearance of more than one boundary or peak in the Schlieren diagram would be a clear indication of the existence of two types of molecules in the system. We have also used this method for the investigation of association in PVC.

As has already been mentioned in the introduction chain scission and cross linking are the two possible reactions during the degradation of PVC. An ultracentrifuge could be a very good tool for the investigation of structural changes in PVC during degradation. (Sedimentation would be slow if chain scission were taking place and would be faster if cross linking were to occur). No previous investigations have been carried out with an ultracentrifuge to explore the degradation. An attempt was therefore made here to follow the degradation by this method.

## Experimental

Solvent Cyclohexanone (B.D.H. grade) was fractionally distilled at atmospheric pressure and the fraction boiling between 154°C - 156°C was used.

Preparation of solution The solution was prepared by dissolving a known weight of polymer in cyclohexanone. The solution was left for 20 - 24 hrs. at room temperature to dissolve the polymer. It was then heated for 30 minutes between 70° - 100°C

and finally made upto the required volume at 25°C. This standard polymer solution was diluted with appropriate volumes of solvent, and thus 4 or 5 polymer solutions of different concentrations were prepared.

Degradation of polymer. The polymer was degraded at 178°C in sealed tubes. A calculated quantity of polymer was weighed directly into a thick walled glass tube, sealed at one end, and with a B-14C joint and a constriction for sealing off at the other end. 10 ml. of cyclohexanone was added to it and the solution was degassed on the vacuum line by successively freezing, evacuating and thawing three times. The tube was then sealed off at the constriction, and heated in a vapour jacket for the required time.

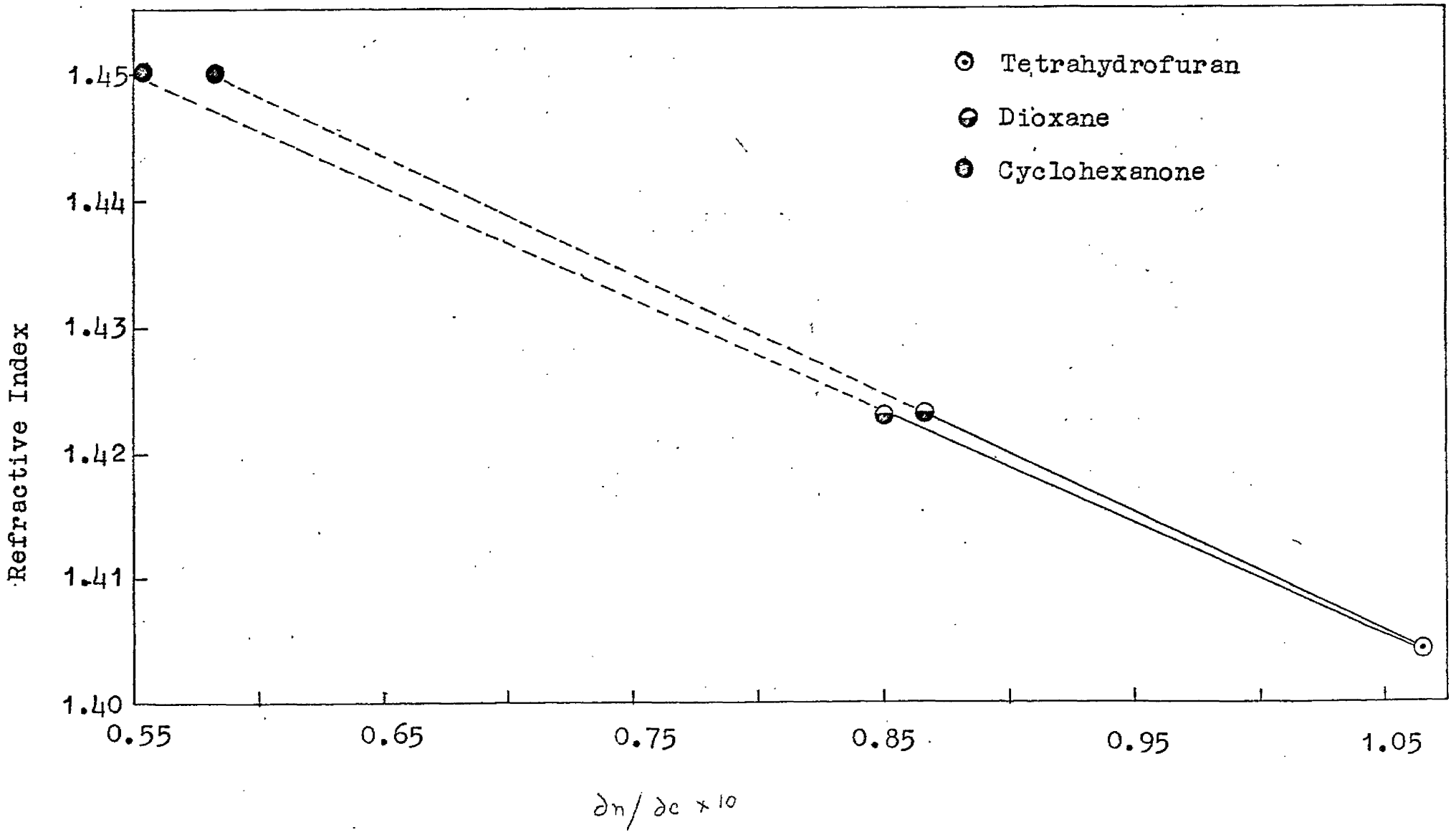
After heating, the tube and contents were cooled to room temperature and then opened. The contents were transferred to a 100 ml. volumetric flask, and the tube was rinsed several times with freshly distilled cyclohexanone. All the washings were collected in a 100 ml. flask, and then the volume was made upto the mark. This standard polymer solution was diluted in the usual manner to give from three to five solutions of different concentrations.

Molecular weight determination by light scattering

This involves three steps.

(1) Measurement of the refractive index increment.

Fig. 42. Gladstone Dale relationship plot



(2) Clarification of the solution.

(3) Measurement of the intensity of scattered light.

(1) Refractive index increment ($\partial n/\partial c$)

For the correct interpretation of light scattering data, an accurate measurement of the refractive index increment ($\partial n/\partial c$) is of utmost importance, because it appears as a squared term in the Debye equation (see eq.11). The values quoted in the literature for the cyclohexanone PVC system are not constant and some workers have not given any values[79]. Moore[81] has mentioned a value of 0.0867ml.gm.$^{-1}$ while the value of Wippler, given in the Sofica handbook is 0.0782. From the known values of $\partial n/\partial c$ in different solvents (tetrahydrofuran and dioxane) the Gladstone and Dale relationship plot[87] gave a value of 0.055-0.058 (fig. 42). Because of this variability it was decided to measure this quantity using a Rayleigh interferometer.

The instrument was calibrated by using sucrose solution since its $\partial n/\partial c$ value is more reliable. A value of 0.001417 100 ml.gm.$^{-1}$ was obtained (Lit. value[88] = 0.001430 100 ml.gm.$^{-1}$)

The measurements with PVC cyclohexanone were done at room temperature (18°C - 20°C). The temperature coefficient of refractive index increment is usually small[87], so the values thus obtained would apply at 25 - 26°C, the temperature at which the light scattering measurements were made.

The solution concentration ranged from 0.1 to 0.8 gm. 100 ml.$^{-1}$

Green light (5461° A) was isolated by suitable filter from the Hg lamp and the measurements were made at this wavelength. It was observed that even a slight variation in the temperature between the solution and the solvent compartments resulted in the formation of curved fringes. Sufficient time was therefore, given to attain temperature equilibrium. Another drawback associated with this system is the tendency of cyclohexanone to absorb water. This results in a slight increase in the value of refractive index increment with time. The values obtained varied between 0.069 - 0.075 $ml.gm.^{-1}$ The mean average value of 0.072 $ml.gm.^{-1}$ was then taken as the correct one. This value is similar to the value 0.071 $ml.gm.^{-1}$ obtained by the Distiller's Company (private communication) and by Kratochvil[82] (0.074 $ml.gm.^{-1}$).

The $\partial n/\partial c$ measurements were carried on, JLB-320 (emulsion polymer) JLB-49 (Geon III), precipitated PVC (obtained by total precipitation of JLB-49 from THF solution by methanol) and on samples of precipitated PVC degraded for 10 and 30 mins. The values obtained were similar with slight variations and hence 0.072 $ml.gm.^{-1}$ has been used for the interpretation of data.

Clarification of solutions. The presence of dust particles in the solution causes an increase in the intensity of the scattered light and has a marked influence on its angular

distribution. Therefore the removal of the dust from solutions is of utmost importance.

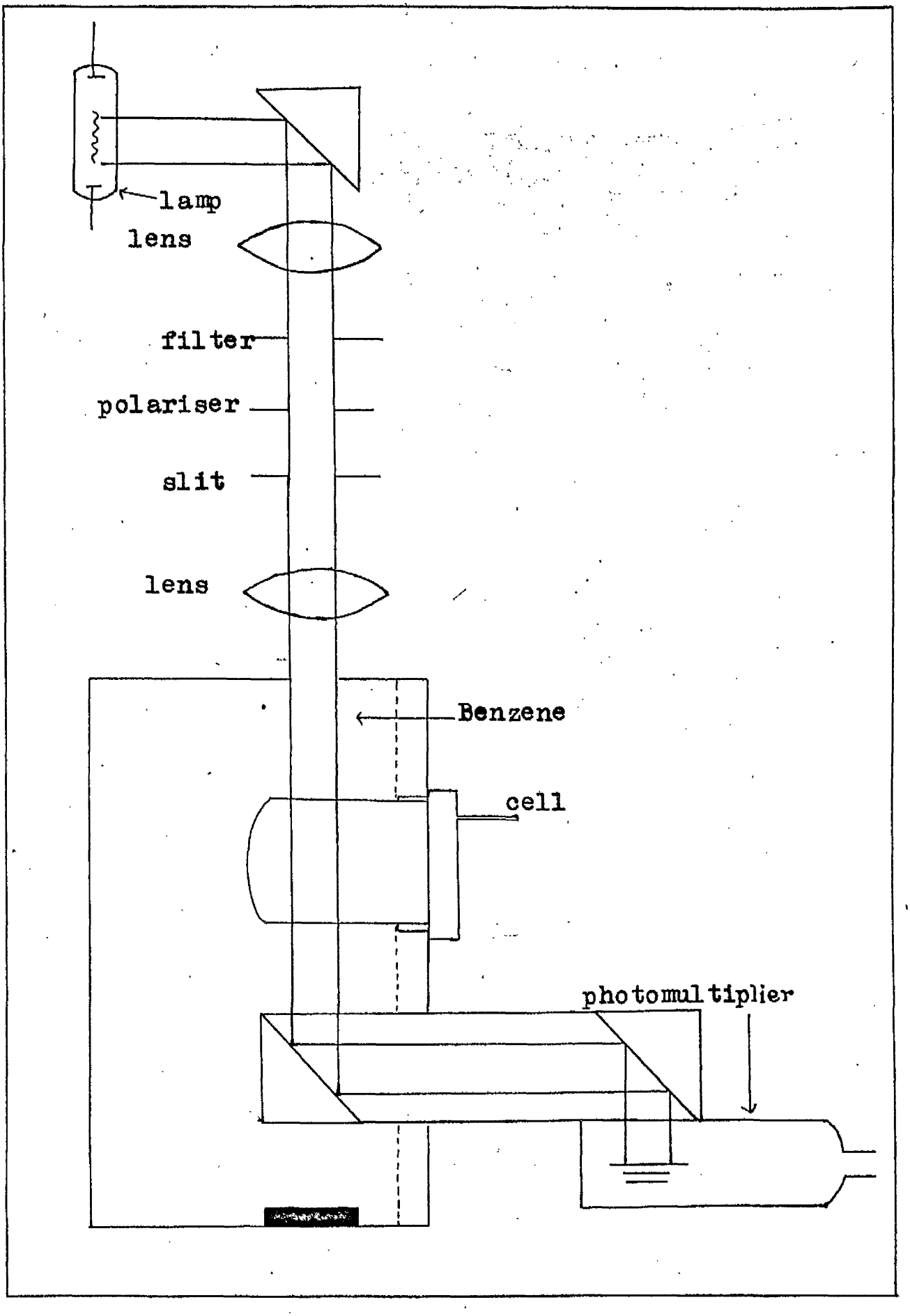
In this work centrifugation was employed as a means for clarifying the solutions, since preliminary attempts using millipore filters proved unsuccessful.

A M.S.E 'high speed 18'' refrigerated centrifuge having an angle type head was used. The polymer solutions (as already prepared) were transferred into the stainless steel centrifuge tubes and were covered by metal tops. The pairs of tubes were balanced to within 0.1 g. before placing them in the centrifuge. Usually 40 ml. of solution was placed in each tube and 5 tubes containing solution and one having solvent were centrifuged for 150 mins. at 25°C - 27°C at a speed of 16000 - 18000 r.p.m. This corresponded to a force of about 29000 to 38000 times that of gravity.

After centrifugation, about 25 ml. of solution was pipetted out and transferred to the light scattering cells by means of clean pipettes. Special care was taken to prevent the contamination of the clean solution with dust during this transfer.

Cleaning of the cells The glassware (cells, pipettes etc.) were rinsed with the solvent, acetone and water. They were, then steeped in a chromic acid - $H_2SO_4$ mixture for at least 4 hrs., washed with tap water, followed by distilled water, and finally dried in an oven at 100°C.

Fig. 43 Light Scattering Apparatus.



The stainless steel centrifuge tubes were similarly rinsed with solvent, acetone and water containing detergent. Finally they were rinsed with tap water and dried in an oven.

Measurement of the intensity of the scattered light

The measurements were carried out with a Sofica Photo Gonio Diffusometre. The principal arrangement of the instrument is shown in fig. 43. The characteristic feature of this instrument is that the scattering cell is suspended in a bath of benzene. This eliminates the large refraction effects at the outside surface of the cell. A water cooled mercury vapour lamp was used as the source of light and the green light of wavelength 5461° A was isolated by means of filter.

The measurements were made with unpolarised light and at eleven predetermined angles (30°, 37.5, 45°, 60°, 75°, 90°, 105°, 120°, 137°, 142.5, 150°).

Standardisation of the instrument The manufacturers had standardised the instrument using dust free benzene. The instrument was then checked in the laboratory using dust free benzene (obtained either by several slow distillations of benzene or by centrifugation). The values given by the manufacturers were obtained. The scatter from a standard cylindrical glass block was measured at 90°and compared with the benzene value. In all subsequent measurements this was used as a secondary standard. The ratio of the scatter of the glass standard to that of clean

benzene was found as 1.06. The performances at other angles of the instrument were tested from time to time by using dust free benzene.

Evaluation of data weight average molecular weight $\bar{M}_w$, the principal dimension (radius of gyration and mean square end to end distance) and the second virial coefficients are usually determined from light scattering data. Number average molecular weight can also be determined if certain conditions apply. The results were evaluated using the method of Zimm[89], which enables all the measured data to be represented graphically and all of the above mentioned quantities to be determined directly.

The intensity of scatter for the solvent ($I_o$) was substracted from the intensity of scatter for solution I. The values thus obtained ($I - I_o$) were multiplied by the coefficient $\frac{\sin\theta}{1 + \cos^2\theta}$. This is to take into account the variation of the diffusing volume in terms of angles and the polarization of the diffused light.

$$I_s = (I - I_o) \times \frac{\text{Sin}\,\theta}{1 + \cos^2\theta} \qquad (10)$$

Finally the $c/I_s$ value was calculated for each angle and concentration.

The data were plotted as $c/I_s$ against $k_1C + \sin^2\frac{\theta}{2}$ where $k_1$ is an arbitrary constant used to obtain an open display of the data. The grid like plot was then simultaneously

extrapolated along lines of constant angles to zero concentration and along lines of constant concentration to zero angle. The two new lines (zero angle and zero concentration) thus obtained should meet on extrapolation at the same intercept on the ordinate. This extrapolated value is used in the calculation of molecular weight and dimension.

The Debye equation was used to evaluate the molecular weight of the polymer.

$$\frac{K_1 c}{R_\theta} = \frac{1}{\bar{M}_w P_\theta} + 2Bc \qquad (11)$$

where $R_\theta$ is the measured Rayleigh ratio at an angle of $\theta$ to the incident beam

c is concentration gm.ml.$^{-1}$

$\bar{M}_w$ = weight average molecular weight of scattering solute

$P_\theta$ = particle scattering factor

= second virial coefficient

$K_1$ is a constant and is given by

$$\frac{2\pi n_o^2}{\lambda_o^4 N_A} \left(\partial n / \partial c\right)^2$$

where $n_o$ = refractive index of benzene

$\lambda_o$ = wavelength of the light used (5461 $^{o}$A)

$N_A$ = Avogadro's number

$\partial n/\partial c$ = refractive index increment

In equation 11, $P_\theta^{-1}$ is a function of the angle $\theta$ and in the limit $\theta=0$, $P_\theta^{-1} = 1$ so at zero angle and zero concentration

equation (11) is reduced to

$$K_2\left(\frac{C}{I_S}\right)_{\substack{\theta=0\\ C=0}} = \frac{1}{\bar{M}_w} \qquad (12)$$

The constant $K_1$ of equation (11) has been replaced by $K_2$ because the Rayleigh ratio at angle $\theta$ is replaced by intensity of scatter. The intensity of scatter could be converted to Rayleigh ratio, if one correlates it with the intensity of scatter of some other solvent whose Rayleigh constant is known. Benzene was used for such correlation purposes in our experiments.

$$K_2 = \frac{K_1}{R_B} \times I_B \qquad (13)$$

where $R_B$ = Rayleigh constant of standard benzene ($16.3 \times 10^{-6}$ for $\lambda_0 = 5461^{\circ}$A).

$I_B$ = intensity of light scattered at $90^{\circ}$ by standard benzene under conditions of experiment

The value of $\frac{2\pi n_0^2}{\lambda_0^4 N_A R_B}$ is constant for a particular wavelength and is equal to 0.506 for $\lambda = 5461^{\circ}$ A

$$\therefore \frac{1}{\bar{M}_w} = 0.506 \times \left(\partial n/\partial c\right)^2 \times I_B \times \left(\frac{C}{I_S}\right)_{\substack{\theta=0\\ C=0}} \qquad (14)$$

Radius of gyration $\langle \bar{r}^2 \rangle_z$ When C = 0, equation (11) has the form

$$K_1\left(\frac{c}{R_\theta}\right)_{c=0} = \frac{1}{\bar{M}_w P_\theta} \qquad (15)$$

It has been shown that at low values of $\theta$

$$P_\theta^{-1} = 1 + \frac{u^2 \bar{\rho}^2}{3}$$

where $\bar{\rho}^2$ = mean square radius of gyration

$$u = \frac{4\pi}{\lambda'} \sin\frac{\theta}{2}$$

$$\lambda' = \frac{\text{wavelength of light in vacuum}}{\text{refractive index of solution}}$$

Substituting the values of $P_\theta^{-1}$ in equation (15)

$$K_2\left(\frac{c}{I_s}\right)_{c=0} = \frac{1}{\bar{M}_w}\left(1 + \frac{16\pi^2}{\lambda'^2}\frac{\bar{\rho}^2}{3}\sin^2\frac{\theta}{2}\right) \qquad (16)$$

The differentiation of $(c/I_s)_{C=0}$ with respect to $\sin^2\theta$ will give

$$K_2 \frac{d\left(c/I_s\right)_{c=0}}{d\left(\sin^2\frac{\theta}{2}\right)} = \frac{1}{\bar{M}_w}\frac{16\pi^2}{\lambda'^2}\frac{\bar{\rho}^2}{3} \qquad (17)$$

$\frac{d\left(c/I_s\right)_{c=0}}{d\left(\sin^2\frac{\theta}{2}\right)}$ is the slope of zero concentration line

$\therefore$ $K_2 \times$ slope of zero concentration line $= \frac{1}{\bar{M}_w}\frac{16\pi^2}{\lambda'^2}\frac{\bar{\rho}^2}{3}$ (18)

In the limit of zero angle and zero concentration

$$K_2 = \frac{1}{\bar{M}_w\left(c/I_s\right)_{\substack{\theta=0\\c=0}}}$$

By substituting the value of $K_2$ in equation (18) and rearranging one gets

$$\frac{\text{slope of zero concentration line}}{\left(c/I_s\right)_{\substack{\theta=0\\c=0}}} = \frac{16\pi^2}{\lambda'^2}\frac{\bar{\rho}^2}{3} \qquad (19)$$

Thus knowing the slope of zero concentration line and intercept on $c/I_s$ axis one can calculate the radius of gyration.

If a perfectly gaussian distribution of segments is assumed then

$$\langle \bar{r} \rangle_z^2 = 6 \langle \bar{\rho} \rangle_z^2 \qquad (20)$$

Thus the Z average mean square end to end distance can be calculated from the Zimm plot. It has been shown that the particle size is a Z average if polymer is heterogeneous[89].

Second virial coefficient The second virial coefficient may be thought of as a measure of the solute - solvent interaction or solute - solute interaction.

When $\theta = 0$ , eq. (11) may be written as

$$K_2\left(\frac{c}{I_s}\right) = 2Bc + \frac{1}{\bar{M}_w} \qquad (21)$$

and from this the value of B or second virial coefficient can be calculated

$$B = \frac{\text{slope of } (c/I_s) = 0 \text{ line} \times K_2}{2} \qquad (22)$$

Number average molecular weight The scattering at larger angles is due more to the smaller molecules. The plot of the angular scattering is therefore curved. The asymptote to this curve at the point of intersection on the ordinate $(K, c/R_\theta)_{\substack{C=0 \\ \theta=0}}$ is equal to the reciprocal of twice the $\bar{M}n$[90]. The ratio of the slope

to intercept yields the number average radius of gyration.

Correction for light absorption in degraded PVC

One of the problems associated with the light scattering measurements on degraded PVC is the development of colour which leads to the absorption of light in the region where such measurements are made. Thus, if we do not correct for absorption a low estimation of the molecular weight will be obtained.

The intensity of the incident beam is reduced by absorption in the coloured media, and similarly the intensity of scattering light is decreased before it reaches the cell walls. Thus the observed value of scatter would be low, and the real value could only be obtained by dividing the observed value with the transmittance of solution.

From Beer's Law of light absorption we know that

$$I = I_o \, e^{-acd} \qquad (23)$$

where $I$ = intensity of light transmitted

$I_o$ = intensity of incident light

$d$ = the path length of the light

$c$ = concentration

$a$ = absorptivity or extinction coefficient

from eq. (23) transmittance would be

$$\frac{I}{I_o} = e^{-acd} \qquad (24)$$

This equation (24) is generally used with base 10 and so,

$$\frac{I}{I_o} = 10^{\frac{a}{2.303} cd} \qquad (25)$$

Putzeys and Dory[91] and Brice et. al.[92] have also studied light scattering by coloured solutions. The other corrections which they have applied have been neglected here since we have used a narrow slit width, and have suspended the scattering cell in a vat of benzene, to avoid refraction at the air glass interface.

The inside diameter (d) of the scattering cell was measured with a telescopic gauge and micrometer and was found to be 2.75 cms. The absorbance ($\log_{10}\frac{I_o}{I}$) was measured using a Perkin-Elmer spectrophotometer. Since the concentration of chromophoric groups is not known, it is assumed that the concentration of such species per gm. of polymer is constant.

The following table shows a typical correction as applied to a coloured solution.

Table 20

PVC degraded 90 mins at 178°C
Concentration = 0.1027 gm 100 ml.$^{-1}$

Absorbance = 0.04 (in one cm. cell) at 546 m u

| Scatter \ Angle | 30° | 45° | 60° | 90° | 120° | 135° | 150° |
|---|---|---|---|---|---|---|---|
| observed value | 197 | 118 | 81.8 | 61.8 | 78 | 105 | 162 |
| correct value | 252.2 | 152.2 | 104.7 | 79.8 | 100.6 | 135.5 | 209 |

Thus an error of 28.9% is introduced if the values are not corrected for absorption.

Fig. 44 Spinco Model "E" Ultracentrifuge Diagramm.

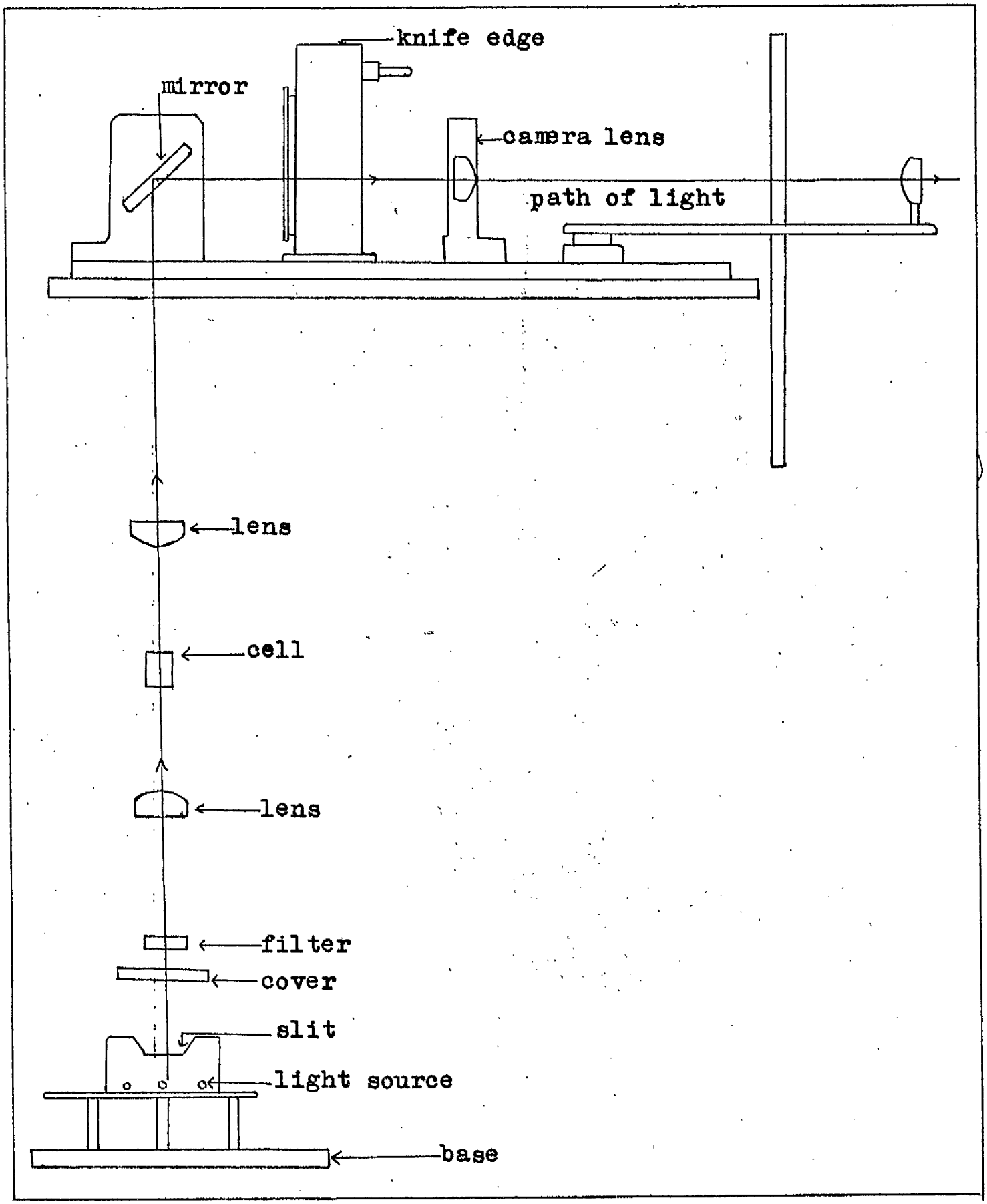
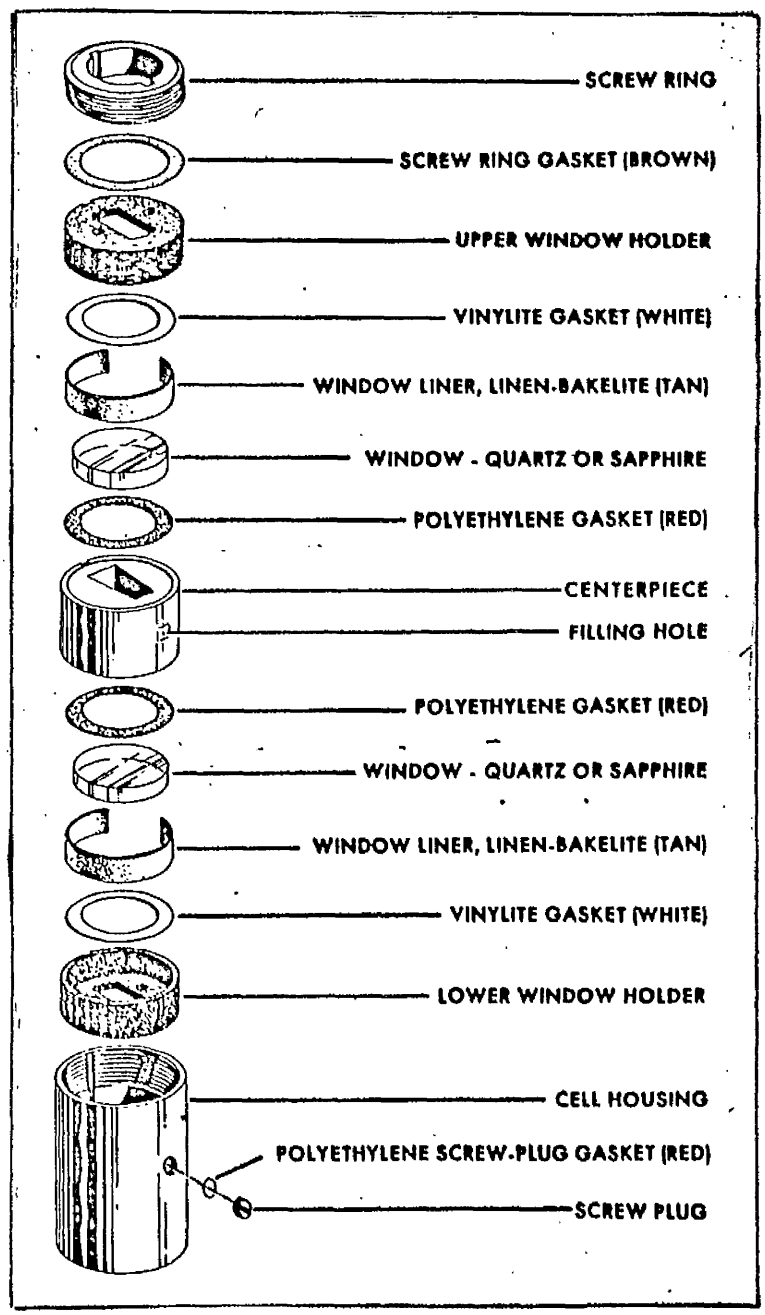


Fig. 45 The cell assembly



Ultracentrifuge measurements

A spinco Model E, Beckmann Analytical Ultracentrifuge was used. An An-D type of rotor having two cell holes (for holding one cell and a counter balance) and spinning upto 59,780 r.p.m. was used. At the top of the rotor was the support ring which held the rotor on to the fork while it was being attached to the drive shaft. At the bottom of the rotor was a thermistor needle, the resistance of this varied with temperature. This delicate needle was protected by a stand when the rotor was not being used, and when in use, the needle completed the circuit to the temperature control unit, by making contact via a pool of mercury. A diagrammatic sketch of the ultra-centrifuge is given in fig. 44.

A standard 12 mm., $4^{\circ}$ sector shaped cell was used. The sector shape of the cell minimises the convective current inside the solution. The cell consisted of an aluminium centrepiece, two quartz windows and two window holders. These five parts were assembled into the cell housing with various gaskets as is shown in fig. 45. A screw ring top helped to hold these things tightly in position,

The cell was filled, while being kept in a horizontal position, with a syringe needle which was inserted through a small opening in the cell housing and centrepiece. A tiny air bubble left inside provided the meniscus. The opening was

closed by screwing a small plug together with a polyethylene gasket.

A counterbalance with brass plug was used to balance the cell. Its weight was adjusted to be either equal to or slightly less than (upto 0.5 gm.) that of the cell. There were two holes in the counterbalance which formed images of undeviated light just beyond the inner and outer edges of the sector opening of the cells.

The counterbalance and cell were then placed in the rotor, after applying some Spinkote grease to the walls. The holes on the rotor were numbered, and cell was always placed in no. 1 hole. The lines at the bottom of the cell and counterbalance were aligned with the lines marked on the rotor. This alignment is critical, since it checks the convection during centrifugation[93].

After loading the rotor, it was attached to the drive shaft and the chamber was closed. The vacuum pump and later on the oil diffusion pump were started. The ultracentrifuge was usually operated at the vacuum which varied between 0.5 - 4 micron. This vacuum lowers the frictional forces which would otherwise develop an intense heat. When the required vacuum was obtained the light source (which was a water cooled mercury vapour lamp) was switched on and the rotor started. All these runs were done at room temperature.

The rotor attained the required maximum speed in about 9 - 14 mins. The photographs were taken after it had attained the maximum speed. An exposure time of 10 - 15 secs. was used and the photographic interval varied from 4 minutes to 16 minutes, depending upon the sample under investigation.

Evaluation of data

The sedimentation coefficient is defined[94] as the proportionality constant relating the mass transported across a surface per unit time , to the concentration at the surface, the area of the surface and the magnitude of centrifugal field.

$$Sc = \frac{dx/dt}{\omega^2 x} \qquad (26)$$

where Sc = sedimentation coefficient

$\omega$ = angular velocity

x = distance between particle and centre of rotation

t = time

Angular velocity could be determined by

$$\omega = 2\pi \left(\frac{\text{r.p.m.}}{60}\right) \qquad [\text{sec.}^{-1}] \qquad (27)$$

The rotation per minute (r.p.m.) used in our experiment was 59,780 which corresponded to a centrifugal force of 259,700 times of gravity.

The unit of sedimentation coefficient is the Svedberg and one Svedberg = $10^{-13}$ sec.

The distance travelled by the boundary or peak was measured

from photographic plate using a cathetometer (reading down to 0.001 cm.). The photographic plate was stuck vertically on an illuminated glass surface by means of cellotape. The distances thus measured are greater than the real dimension in the ultracentrifugal cell. The magnification ($M_A$) was determined by measuring the distance between the two reference holes on the photographic plate and dividing by the real cell dimension (as noted in the instruction book.) The magnification factor $\frac{1}{M_A}$ slowly increased from 0.466 - 0.471. This increase is probably due to deformation of the cell which becomes slightly elliptical under the influence of a high centrifugal force.

There are three ways of evaluating the sedimentation coefficient from eq. (26)

(1) Differential form of eq. (26)

According to this

$$Sc = \frac{x_2 - x_1}{\frac{x_1 + x_2}{2} (t_2 - t_1) \omega^2 60} \qquad (28)$$

(2) Integrated form of eq. (26)

This would lead to

$$sc = \frac{2.303}{\omega^2 60} \frac{\log x_2 - \log x_1}{t_2 - t_1} \qquad (29)$$

(3) Graphical Extrapolation In this method log x is plotted against time. The slope of the resulting line on multiplication

by $\frac{2.303}{60\omega^2} = 9.8 \times 10^{-10}$ yields the sedimentation coefficient.

The graphic evaluation of Sc is the easiest and quickest way of calculation, but the objection to this method is the impossibility of detecting a variation in Sc with time. This variation could either be due to change in concentration or hydrostatic pressure, and requires a correction.

It was, therefore, decided to evaluate Sc using the graphical method as well as the differential method using eq. (28). In table 21 the result of both the calculations are given

Table 21

Sedimentation coefficient determination of precipitated PVC

Solvent - tetrahydrofuran, conc. = 0.00759 gm.ml.$^{-1}$

Magnification ($M_N$) = 2.141, $\frac{1}{M_A}$ = 0.467, centrifuge attained maximum speed in 9 mins 30 secs., position of meniscus from centre of rotation = 5.9956 cms.

| No. | Time (t) mins. | $\bar{x}$ cms. | $\Delta t$ | $\Delta x$ | $\frac{x_1+x_2}{2}$ | Sedimentation coefficients |
|---|---|---|---|---|---|---|
| 1 | 0 | 6.0157 | | | | |
| 2 | 50 | 6.2086 | 50 | 0.19286 | 6.1121 | 2.68 |
| 3 | 82 | 6.3188 | 32 | 0.11021 | 6.2636 | 2.35 |
| 4 | 114 | 6.4425 | 32 | 0.12373 | 6.3806 | 2.60 |
| 5 | 146 | 6.5597 | 32 | 0.1172 | 6.5011 | 2.39 |
| 6 | 178 | 6.6872 | 32 | 0.1275 | 6.623 | 2.56 |
| 7 | 210 | 6.8077 | 32 | 0.1205 | 6.7474 | |

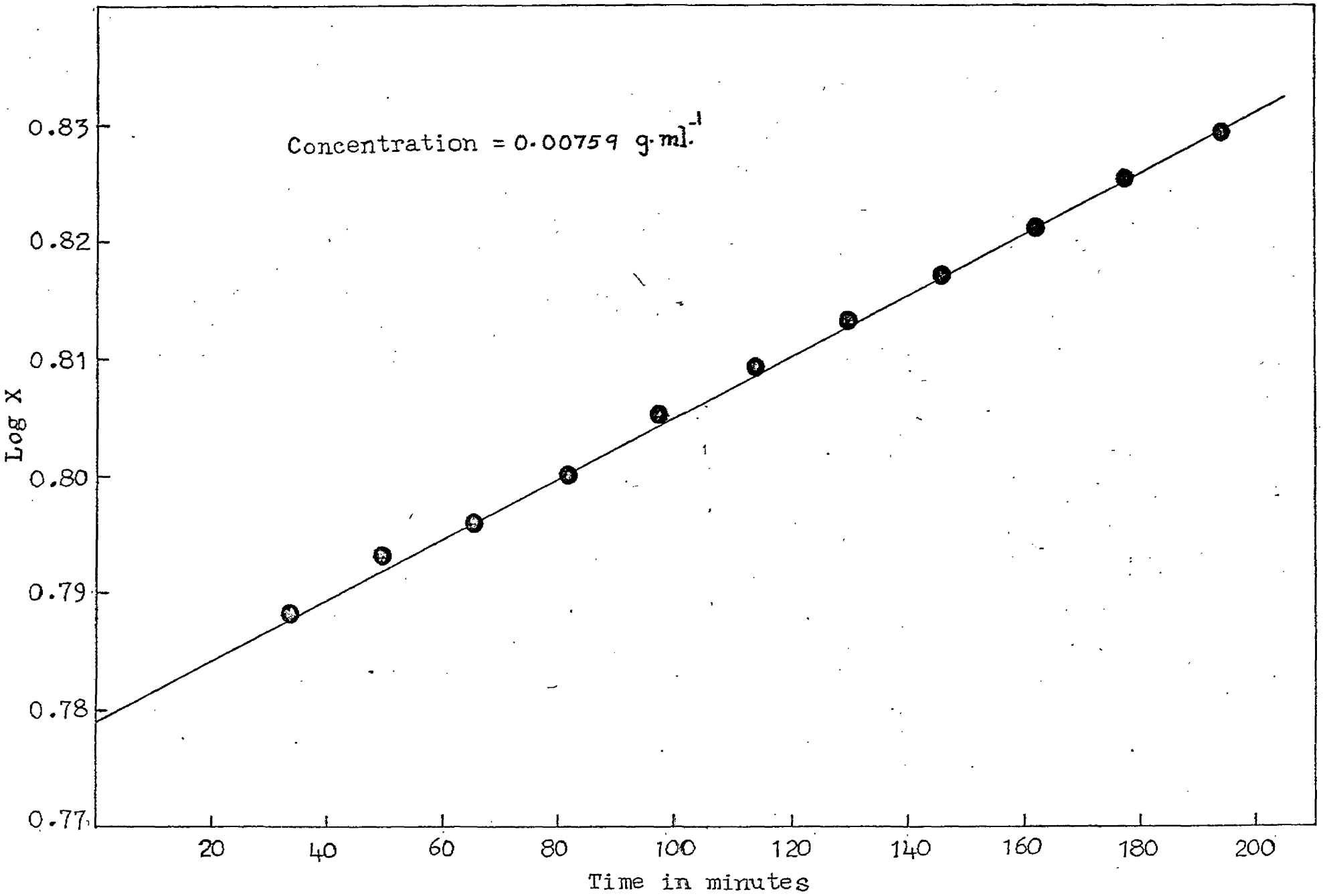



Fig. 46 Graphical evaluation of sedimentation coefficient ( Sc ).

The value of Sc obtained by graphical method (fig. 46) was 2.537 Svedberg, and the mean value of Sc calculated by differential method is 2.522 Svedberg. Furthermore, there is no systematic decrease in the value of Sc calculated by the latter method. Thus the pressure and/or concentration inside the cell are not varying significantly, so no correction is necessary. It was, therefore, decided to use the graphical method of evaluating Sc in subsequent work.

Sedimentation coefficients are determined at a finite concentration of solute and are concentration dependent. The sedimentation constant is defined as the sedimentation coefficient at zero concentration. It could be determined by measuring sedimentation coefficient at 3 or 4 low concentrations (less than 0.7 gm. 100 ml.$^{-1}$) and extrapolating the values to zero concentration.

## Results and Discussion

The typical Zimm plots obtained for the unfractionated polymer, and its four fractions are shown in fig. (47 - 50).

At higher angles the value of $c/I_s$ (and thus $K_1 c/R_\theta$) remains practically unchanged but there is a marked decrease below 90°. This sort of scattering causes a deformation of angular scattering diagrams, which become curved at lower angles. A rapid change in slope at low angles may be either due to presence of dust, to a very wide distribution of molecular

Fig. 47. Zimm plot of PVC (precipitated polymer)

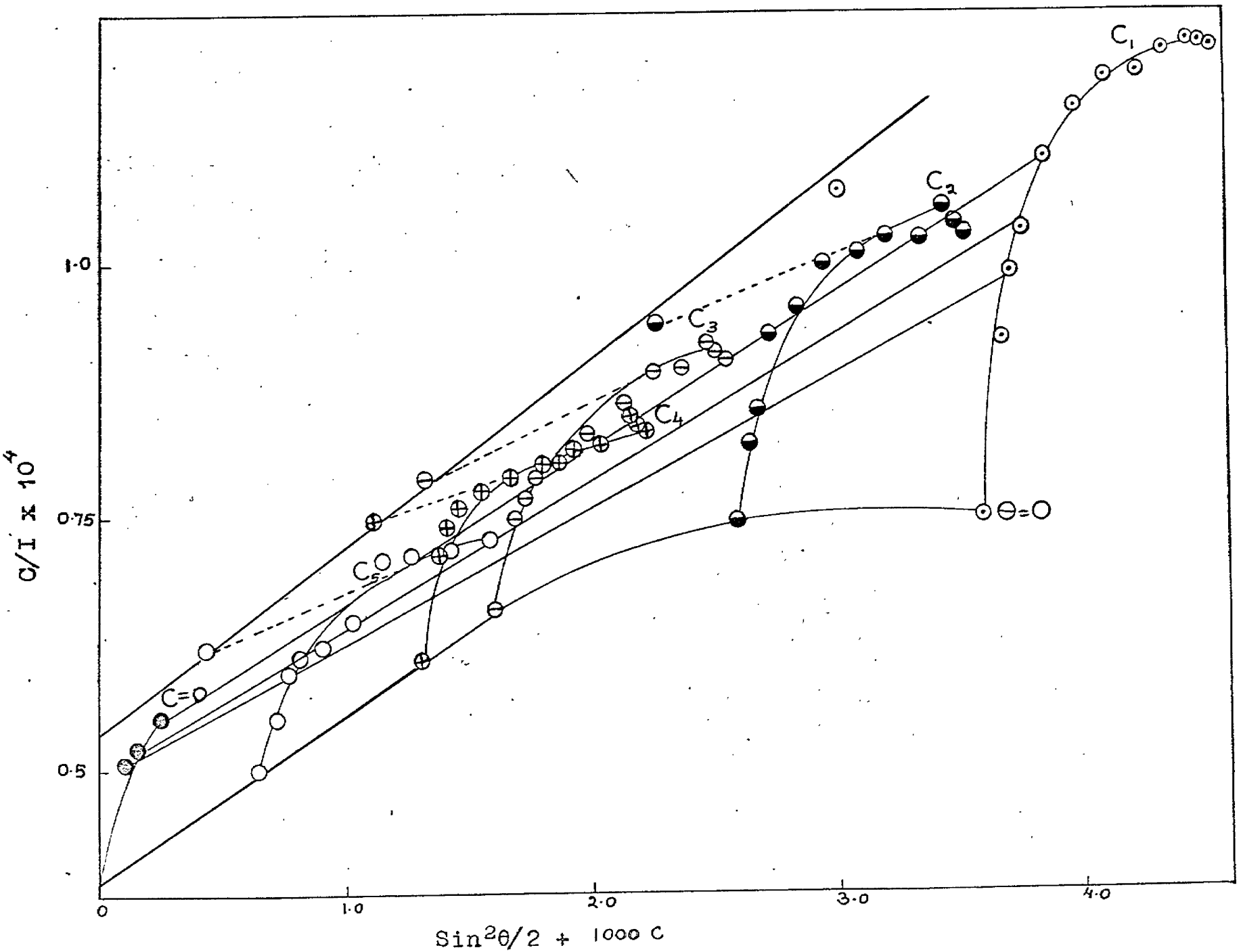
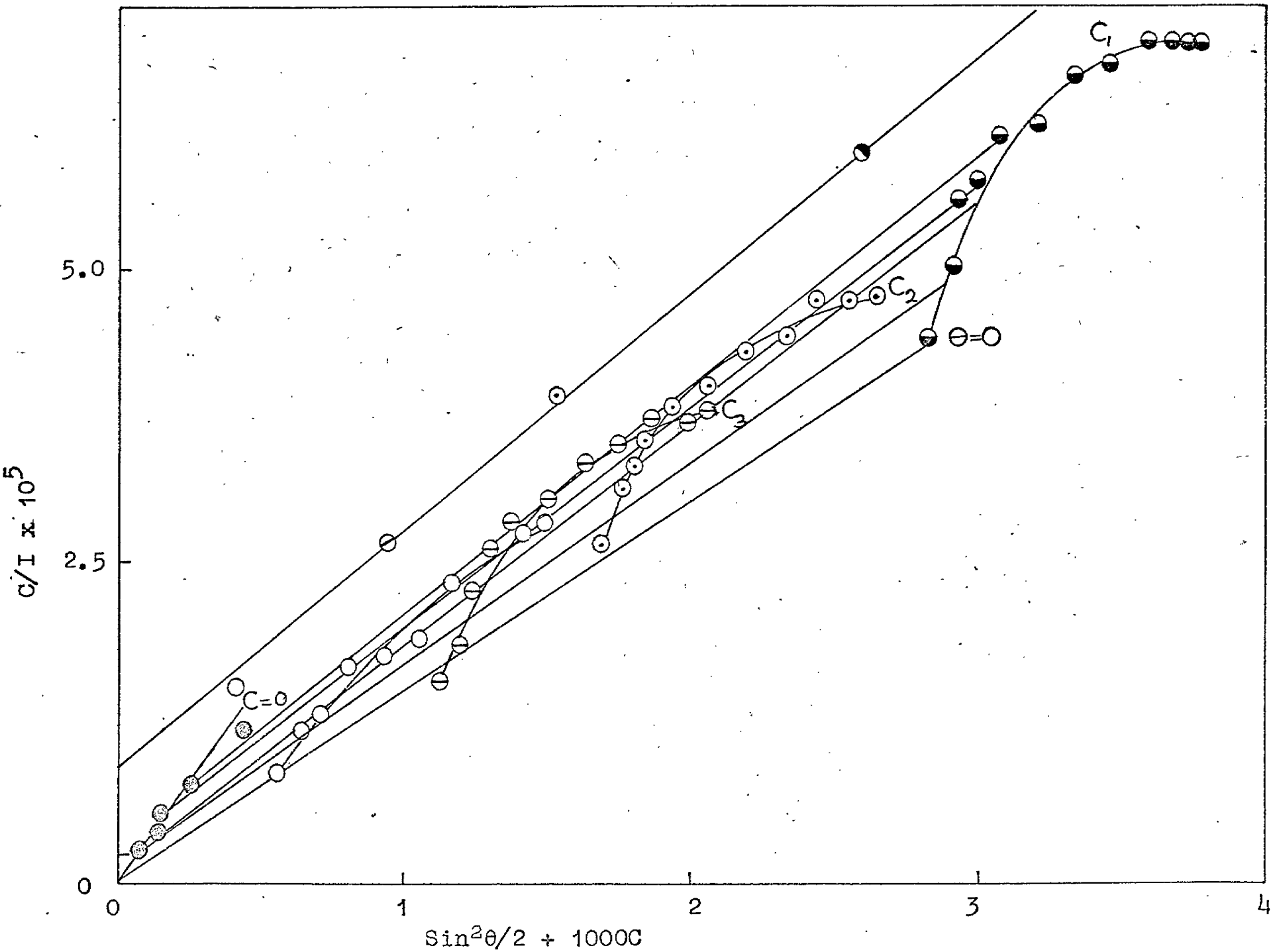


Fig.48. Zimm Plot of Fraction $F_2$ of PVC.



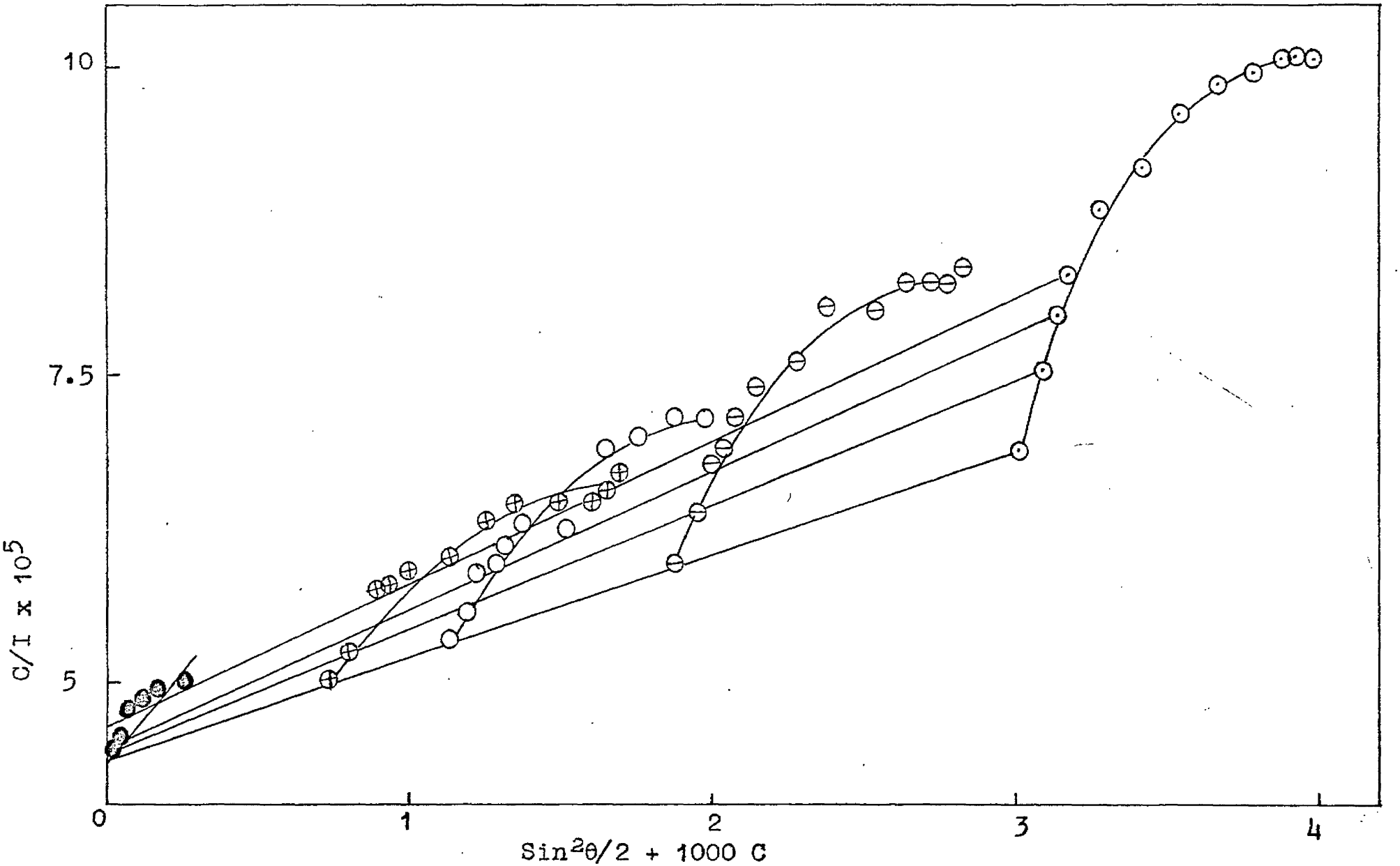



Fig.49 Zimm plot for Fraction $E_4$ ($\eta$=1.125) of PVC.

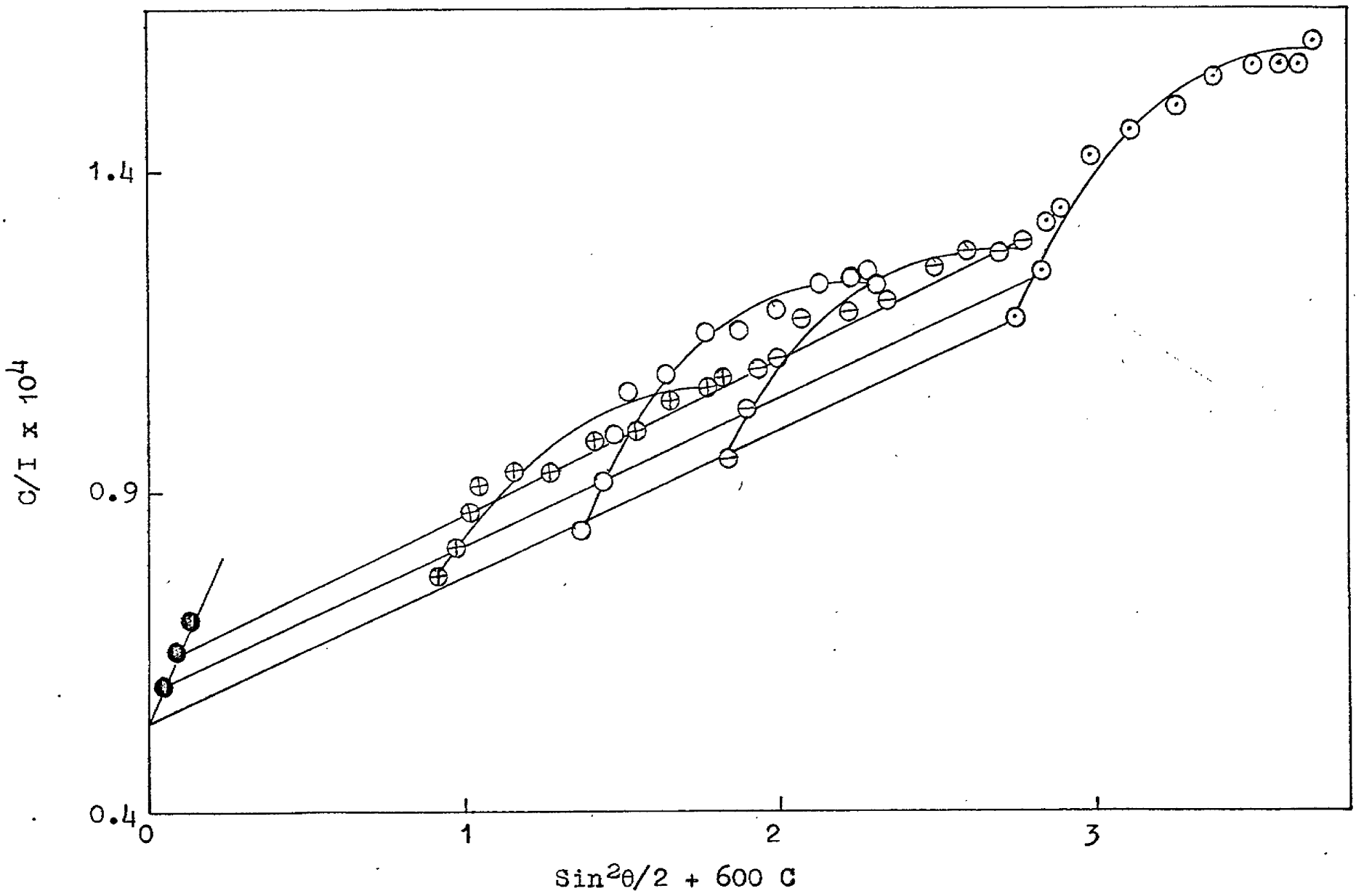
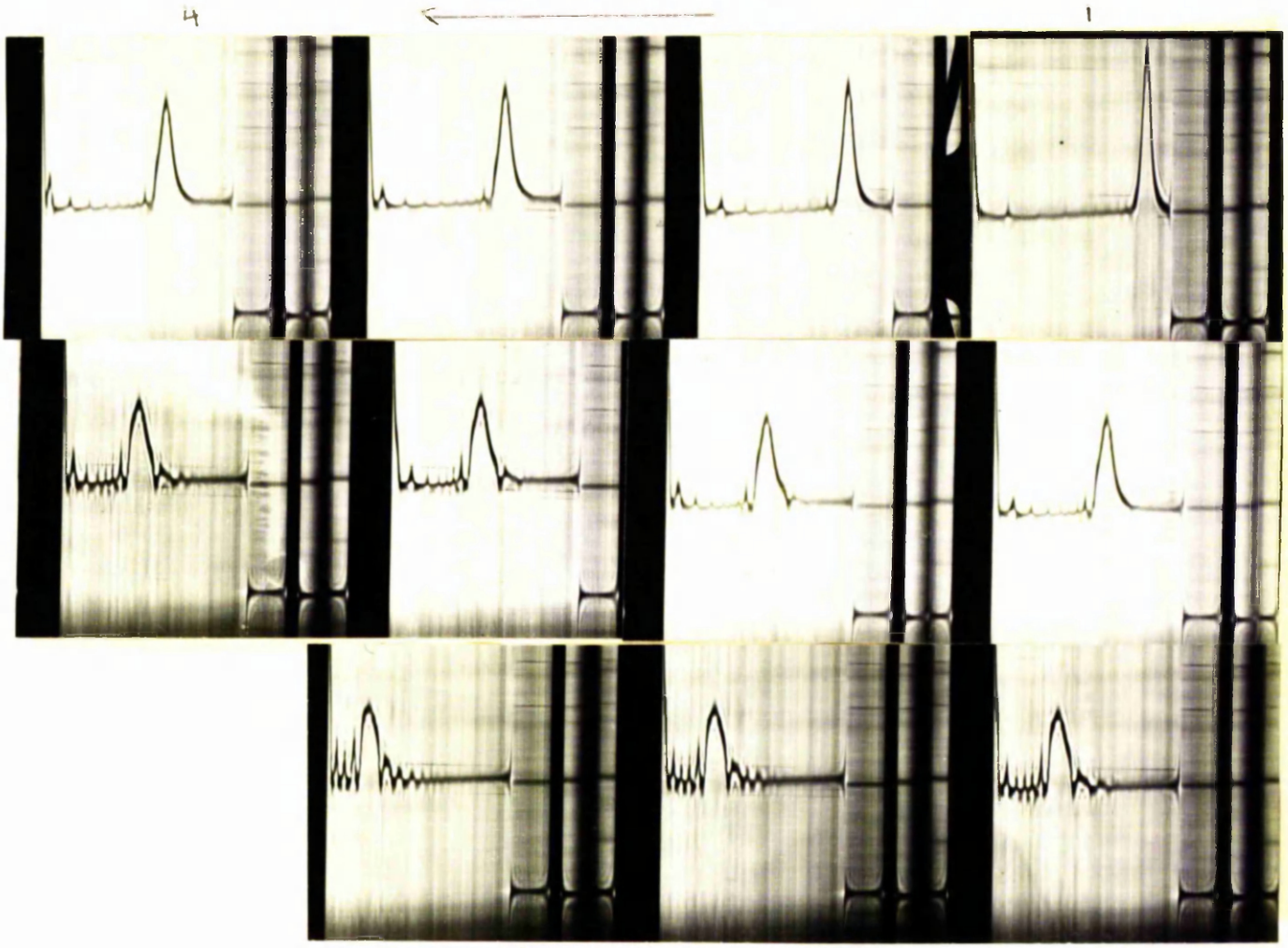



Fig.50 Zimm plot for PVC fraction $F_5$

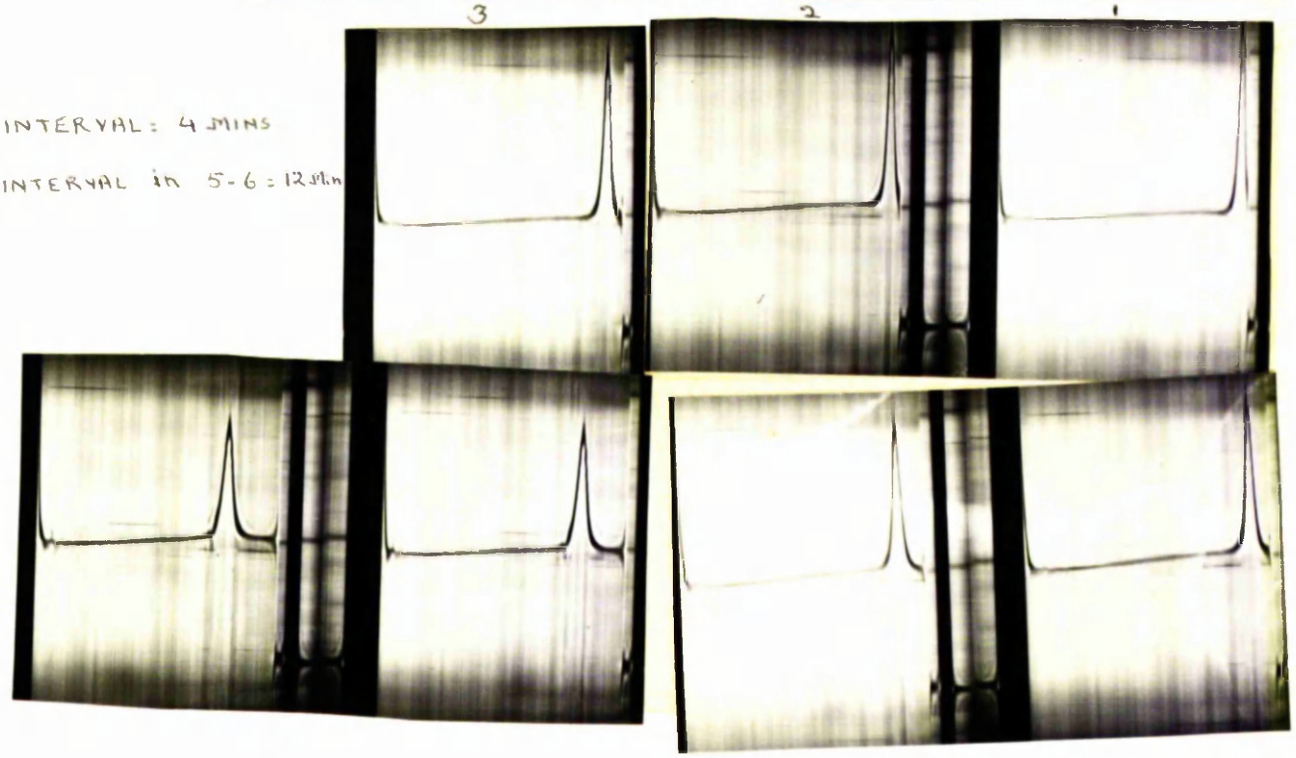
Fig.51 Schlieren diagram for (A) precipitated polymer
B) Fraction $F_4$ ($\eta$=1.125 dl.$g^{-1}$.) of PVC in THF at room temperature. A conc. = 0.759 g.100 $ml^{-1}$.
B conc. =0.548 g.100$ml^{-1}$.
A photo interval 1. 34 mins, 2. 66mins, 16 mins later on.




B

PHOTO INTERVAL: 4 MINS

TIME INTERVAL IN 5-6 = 12 Min



weight[89] or to the presence of microgel.

The presence of dust in the solution could be checked in the light scattering machine by passing a strong beam of natural light through the solution and viewing it at right angles by means of a periscope (the angle selection dial of the machine should be either at very low angle (30°, 37.5) or at high angle 142.5, 150°) since when it is set at 90° the view through the periscope isobstructed.) It was observed that dust if present was in negligible amounts.

An ultracentrifuge run, using the whole polymer (fig. 51) showed the absence of microgel. Since the Zimm plot of the fractions of PVC are very similar to the unfractionated polymer, it was assumed that microgel was absent in all these fractions. Kratochvil[82] has, however, attributed this sort of plot for PVC in cyclohexanone or THF to the presence of microgel. He has reached the conclusion by drawing an analogy with other reported systems e.g. polyethylene[95], polyvinyl alcohol[96], and polyacrylonitrile[97]. This argument of Kratochvil may not be justified, unless it is substantiated by ultracentrifuge data.

The only other possible explanation is that the sample is polydisperse. Benoit et. al.[98] have obtained a similar type of plot for polydisperse cellulose trinitrate. Polyvinyl-chloride prepared by suspension polymerisation is bound to be polydisperse. The curving of the Zimm plots, however, was not

removed even when fractions of PVC were used. Perhaps the fractions are also not homogeneous.

The molecular weights (weight average) calculated from these plots are listed in Table 22, together with the values obtained by using various values of 'K' and 'a' given in Table 19 and substituting them in equation (6).

Table 22

| Authors | Precipitated polymer | $F_2$ $[\eta]=1.32$ | $F_4$ $[\eta]=1.125$ | $F_5$ $[\eta]=0.875$ | $F_6$ $[\eta]=0.615$ |
|---|---|---|---|---|---|
| Fuoss and Mead[54] | 97,000 | 117,000 | 99,000 | 77,000 | 54,000 |
| Ciampa and Schwindt[79] | 100,000 | 120,000 | 102,000 | 79,000 | 56,000 |
| Moore and Hutchison[81] | 123,000 | 172,000 | 129,000 | 82,000 | 43,000 |
| Experimental value | 165,000 | 279,000 | 153,000 | 118,000 | 83,000 |

The experimental value thus obtained are higher than the values calculated from viscosity data. The difference in viscosity average molecular weight and weight average molecular weight may indicate the presence of branching.

The experimental value of $\bar{M}_w$ obtained for the whole polymer ($[\eta]=1.10$) is higher than that of $F_4$ ($[\eta] = 1.125$) of somewhat similar intrinsic viscosity. This behaviour, though

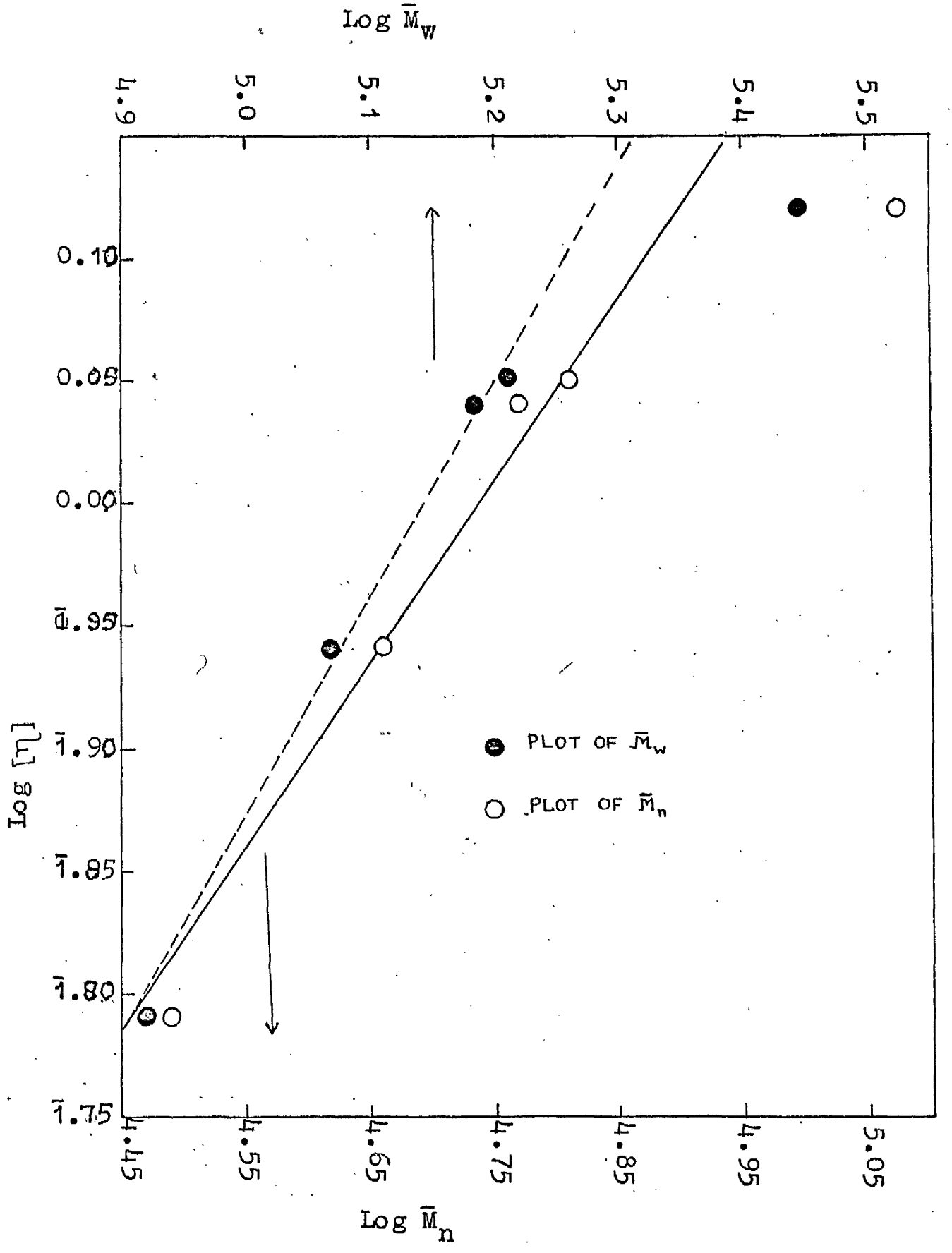



Fig. 52. Mark-Houwink relationship plot for PVC

( Geon 111 )

within the limits of experimental error, is expected because of a wider molecular weight distribution in the whole polymer than in the fractionated sample.

A log log plot of $[\eta]$ vs. $\bar{M}_w$ (fig. 52) enabled us to determine the constants of Mark Houwink equation (6). The slope of the line gave the value of 'a' and from this the value of K was calculated.

$$[\eta] = 2.966 \times 10^{-5} M^{0.88}$$

In this plot we have not taken into consideration the highest molecular weight fraction ($F_2$) because it appears to deviate completely from $[\eta] - \bar{M}$ relationship. Freeman and Manning[80] have also reported that the fraction having a molecular weight above 170,000 do not fall into the line. This could well be attributed to branching in high molecular weight polymer. In free radical polymerisation a growing radical can attack a preformed polymer chain, with the formation of branches. Since the branches would not affect the viscosity very appreciably, but would affect the amount of light scattered by the polymer solution, a high value of $\bar{M}_w$ would be obtained.

Number average molecular weights

The number average molecular weights for various PVC fractions were also determined from the Zimm plots. The values thus obtained together with the values obtained by substituting the value of

'K' and 'a' (as given by various workers) in equation (6) are tabulated in Table 23.

Table 23

The experimental and calculated values of number average molecular weights of PVC fractions in cyclohexanone.

| Authors | Precipitated PVC | $F_2$ | $F_4$ | $F_5$ | $F_6$ |
|---|---|---|---|---|---|
| Bier and Krämmer[51] | 55,000 | 74,000 | 57,000 | 38,000 | 22,000 |
| Mencik[77] | 76,000 | 105,000 | 79,000 | 50,000 | 27,000 |
| Danusso[78] | 53,000 | 72,000 | 58,000 | 42,000 | 27,000 |
| Breitenbauch[76] | 48,000 | 59,000 | 49,000 | 36,000 | 24,000 |
| Hengstenberg[75] | 56,000 | 71,000 | 58,000 | 42,000 | 27,000 |
| Experimental value | 59,000 | 120,000 | 65,000 | 46,000 | 32,000 |

The values of $\bar{M}_n$ thus obtained do not differ much from the values calculated using intrinsic viscosity and molecular weight relationship. The values of $\bar{M}_n$ lie inbetween the value obtained by using Mencik equation, and those of the other workers. A log $[\eta]$ vs. log $[\bar{M}_n]$ plot (fig. 52) gave the following values of 'K' and 'a'

$$K = 1.621 \times 10^{-4}$$

$$a = 0.82$$

Here again, the molecular weight of $F_2$ was higher than predicted by solution viscosity, and in deriving the above relationship this fraction was ignored. Krasovec[99] has also

reported similar deviation from the linear relationship between $[\eta]$ and $[\bar{M}_n]$ for higher avlues of $[\bar{M}_n]$.

The 'a' value for PVC varies from 0.55 - 1 and it has been reported[51,81] that the value of 'a' is less than one if the polymer is branched. The emulsion polymer which may be more branched has lower values of the exponent 'a'[75,77,51,81]. All this indicates branching in the sample used in this work.

The ratio of weight average molecular weight to number average molecular weight gives some idea of the polydispersity of the sample. In Table 24, $\bar{M}_w/\bar{M}_n$, the second virial coefficients, Z average radius of gyration $\langle \bar{\rho} \rangle_z^2$ and Z average mean square end to end distance $\langle \bar{r} \rangle_z^2$ for various fractions are tabulated.

Table 24

The various parameters calculated from light scattering results

| Polymer sample | $\bar{M}_w/\bar{M}_n$ | Second virial coefficient x $10^4$ (B) | $\langle \bar{\rho} \rangle_z^2$ x $10^{-6}$ A | $\langle \bar{r} \rangle_z^2$ x $10^{-6}$ |
|---|---|---|---|---|
| Whole polymer | 3.20 | 5.288 | 0,422 | 2.649 |
| precipitated polymer | 2.77 | 13.062 | 0.678 | 4.071 |
| $F_2$ | 2.32 | 12.708 | 0.364 | 2.181 |
| $F_4$ | 2.26 | 6.414 | 0.181 | 1.082 |
| $F_5$ | 2.57 | 10.745 | 0.552 | 3.312 |
| $F_6$ | 2.61 | 1.068 | 0.269 | 1.616 |

The $\bar{M}_w/\bar{M}_n$ ratio is rather high even for fractions, and indicates a high degree of polydispersity. There is a tendency

for this polydispersity to increase as the molecular weight decreases. The polydispersity of fractions could perhaps be decreased, if smaller fractions were collected. However, this would give insufficient quantities for degradation studies.

Cyclohexanone is thermodynamically a very good solvent for PVC, which is indicated by a high value of second virial coefficient. The extrapolation of the curved Zimm plots to zero angle is accompanied by considerable error, and so the value of B thus obtained appears to bear no relationship to the molecular weight. Generally the second virial coefficient decreases as the molecular weight increases[52]. The value of B should depend upon molecular weight, but Fuoss et. al.[100] have reported that B is independent of molecular weight for poly-4-vinylpyridine. The unsystematic variation of B for PVC in cyclohexanone has also been reported by other workers[82]. The value for B vary in our system from 5.28 - 13.06 (with an exceptionally low value for $F_6$). For a comparison the value of B for other systems is mentioned ee.g. for polystyrene[101] (mol. wt. 286,000) in benzene the value of B is $5.90 \times 10^{-4}$, for polyvinylacetate[102] (mol. wt. 270,000) in acetone $B = 4 \times 10^{-4}$. The value of $12.708 \times 10^{-4}$ for second virial coefficient of $F_2$ (mol. wt. 278,000) indicates that cyclohexanone is a very good solvent for PVC.

The Z average radius of gyration and from this the Z average mean square end to end distance were also determined. The

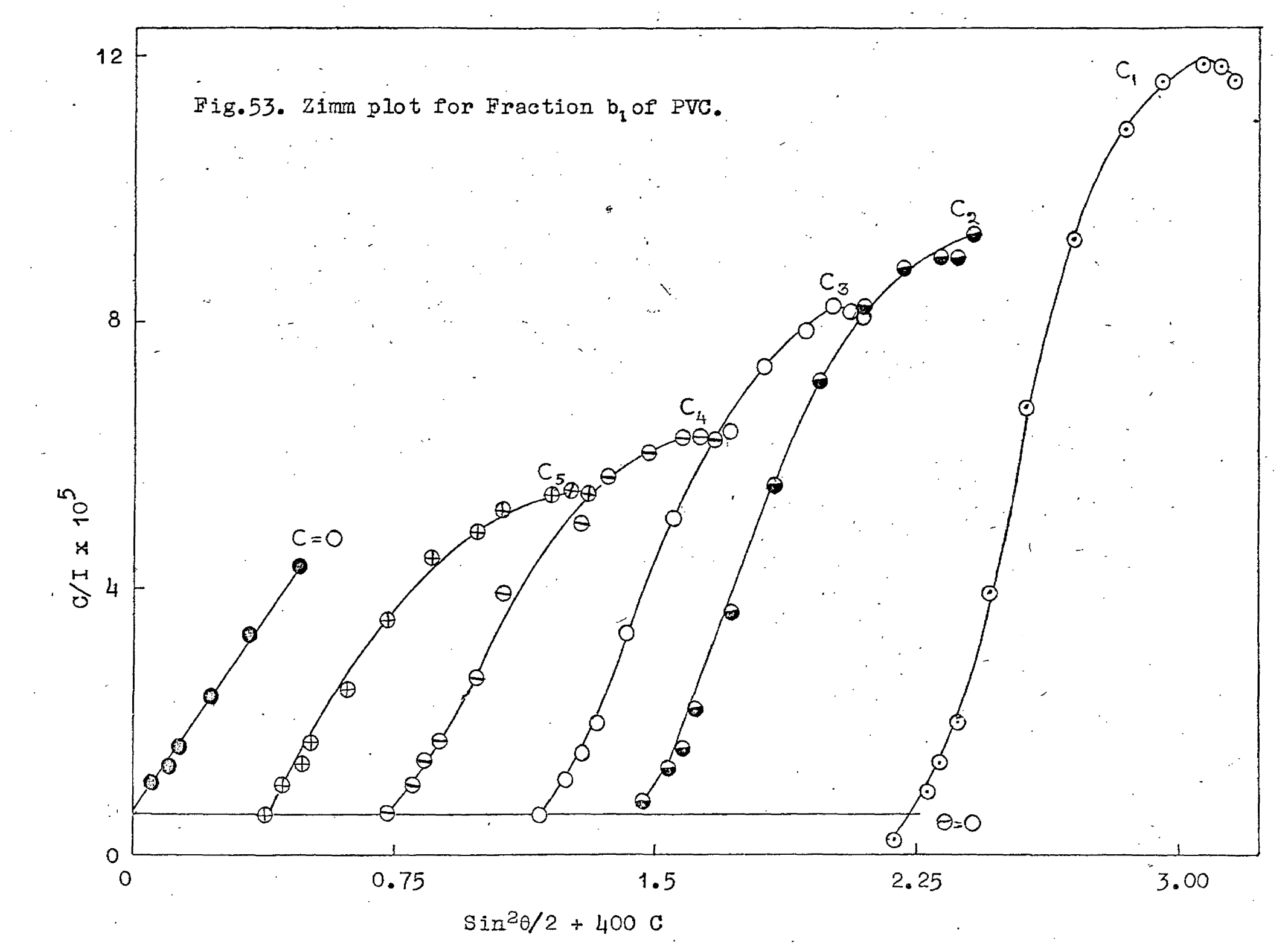


Fig.53. Zimm plot for Fraction $b_1$ of PVC.
12
8
4
0
C/I x $10^5$
0
0.75
1.5
2.25
3.00
$Sin^2\theta/2$ + 400 C
$C_1$
$C_2$
$C_3$
$C_4$
$C_5$
C=O
$\theta$=O

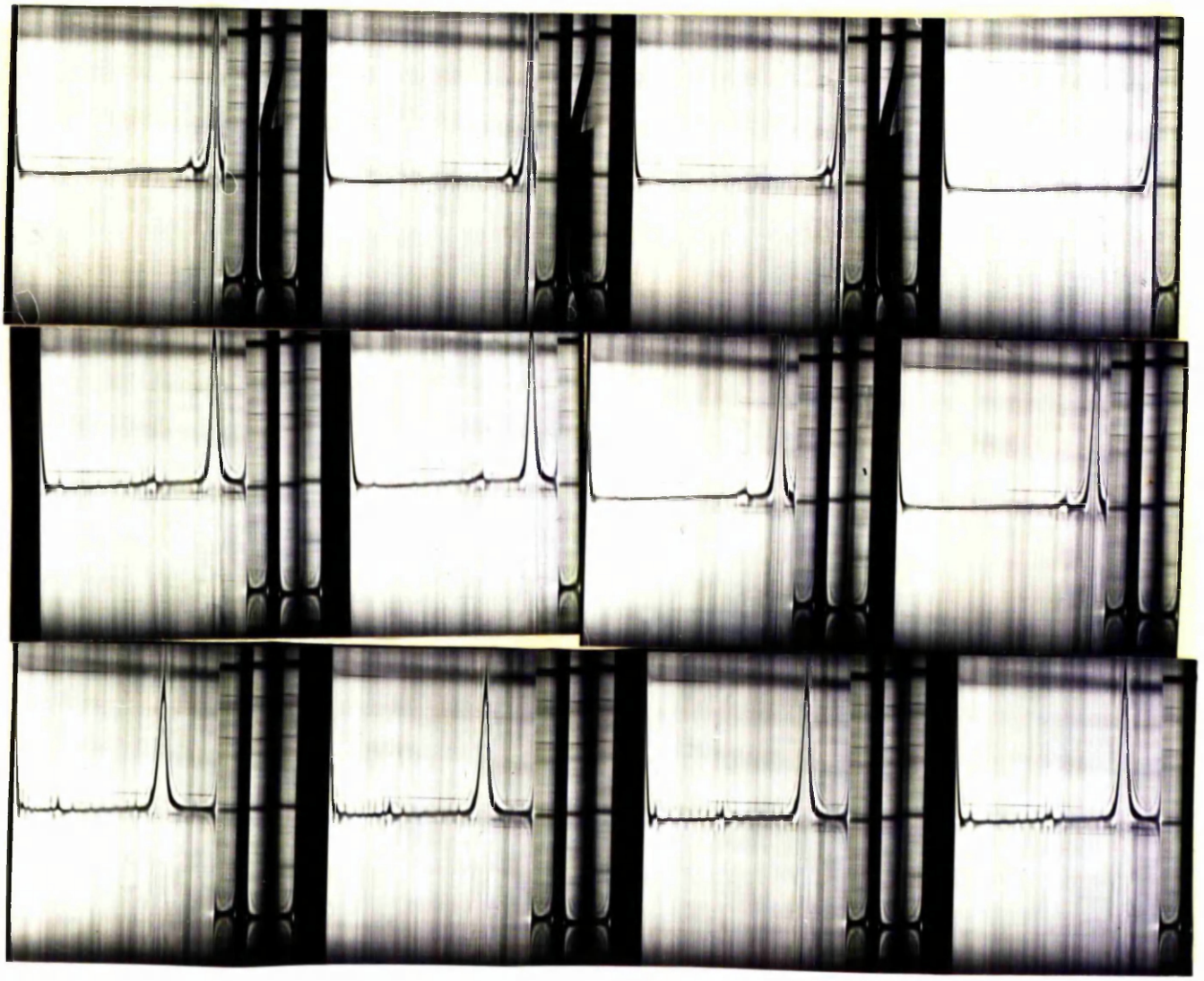
relationship $\langle \bar{r}^2 \rangle_z = 6 \langle \rho \rangle_z^2$ is applicable to coils whose configuration is gaussian. This is achieved when there is no hinderance to rotation at bonds, and the polymer chain is freely jointed. An assumption was, therefore made here that the deviation of segment distribution from gaussian is small. The extrapolation of the constant angle line to zero concentration gives rise to considerable errors due to the high value of the second virial coefficient, and the curving of the Zimm plots. The values of $\langle \bar{r}^2 \rangle_z$ thus obtained appear to bear no linear relationship with molecular weight.

Association of PVC

Two fractions of PVC ($b_1$ and $b_2$) showed association and the Zimm plot for one of these fractions is given in fig. 53.

In these samples the scatter increased even at higher angles. The scattering was unaffected even when the solution was heated for 30 minutes at 90° - 100°C. This behaviour has also been reported by Kratochvil[82] for some of his PVC preparations. This associated PVC or microgel causes a high increase in scatter at lower angles. The presence of microgel in one of these samples was confirmed by ultracentrifuge measurements (fig. 54). The Schlieren diagram indicated the presence of two peaks (1) a small fast sedimenting peak (2) a large peak which represents the unassociated polymer. The sedimentation coefficient for smaller peak at concentration 0.5927 g. 100 ml.$^{-1}$ was 8.575

Fig.54 Schlieren photographs for fraction $b_1$ of PVC showing a fast sedimenting peak (associated polymer) and a slow sedimenting peak. Solvent = THF, Conc. = 0.59 g.100ml.$^{-1}$ Photo interval = 4 minutes for first 6 photos and 8 minutes for others.



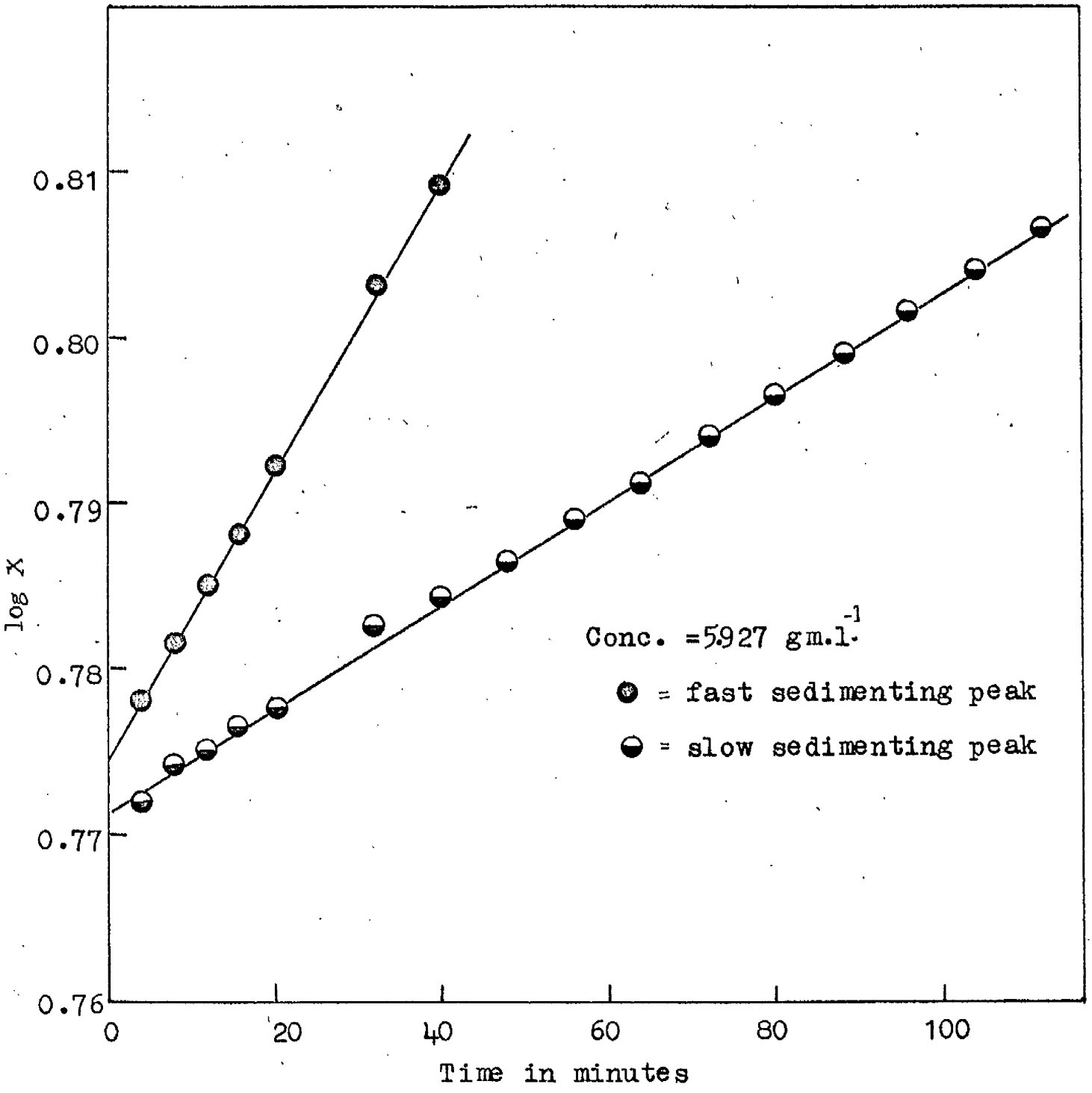


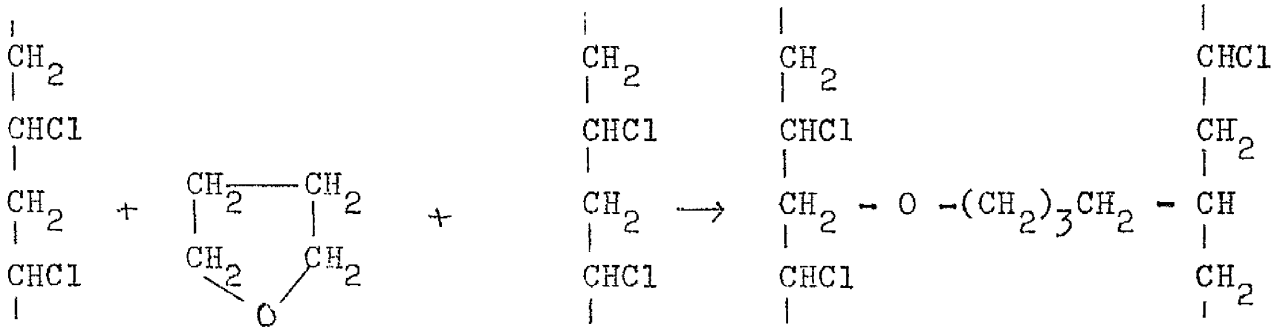

Fig. 55 Sedimentation coefficient determination of PVC fraction ( $b_1$) showing association.

Svedberg and for big peak 3.0743 Svedberg (fig. 55)

These two polymer fractions were obtained by fractionating PVC in tetrahydrofuran (freed from peroxide by refluxing over $FeSO_4$ 7 $H_2O$) with water as precipitant. This was a large scale fractionation, starting from 20 gms. of polymer, 7.48 gms. were collected as the first fraction ($[\eta]$= 1.48) 100 ml. gm.$^{-1}$)and 4.28 gm. as second fraction ($[\eta]$= 0.94 100 ml. gm.$^{-1}$). the $\bar{M}_w$ as calculated from Zimm plots gave a value of 804,000 and 489,000 respectively. The polymer used in this fractionation and also in previous fractionation (when $F_2$,$F_3$ etc. were obtained) was the same. If it is assumed that the first fraction of this should have a molecular weight similar to $F_2$ i.e. 278,000 approximately than the microgel causes a 2.85 times increase in the molecular weight. Incidentally the Sc for the microgel peak was also 2.8 times faster than for unassociated PVC. However only a small fraction of the polymer was in the form of a microgel so this correlation is probably accidental.

It is very difficult to explain why this association had taken place. Doty and Wagner[45] have suggested that association can take place in poor solvent media. Near the precipitation point (as in fractional precipitation) if the polymer is left for a long time association may take place.Mencik[56] observed that association of PVC occurred when THF was used as solvent and methanol as precipitant.

On the other hand, Gautron and Wippler[83] suggest the possibility of hydroperoxide formation in THF which could lead to association. At higher temperatures (50°C or so) the THF ring could open to give a biradical which could serve as a bridge between two PVC molecules. The possible mechanism suggested by Wippler[103] for such opening of ring in case of radio-reticulation of PVC is as follows



These workers observed that sometimes an increase in molecular weight takes place (which means association) if PVC is dried at 50°C or 60°C.

Whether association in our samples arose due to poor solvent media or an active role of the tetrahydrofuran molecule is difficult to judge. Such associations (if not foreseen) could lead to a serious misconception of the molecular weight of the polymer, especially when the light scattering method is used for its evaluation. The intrinsic viscosity (1.48 dl. $gm.^{-1}$) is rather high considering the weight of the fraction collected. Still the indication of association is not so marked as in light scattering studies.

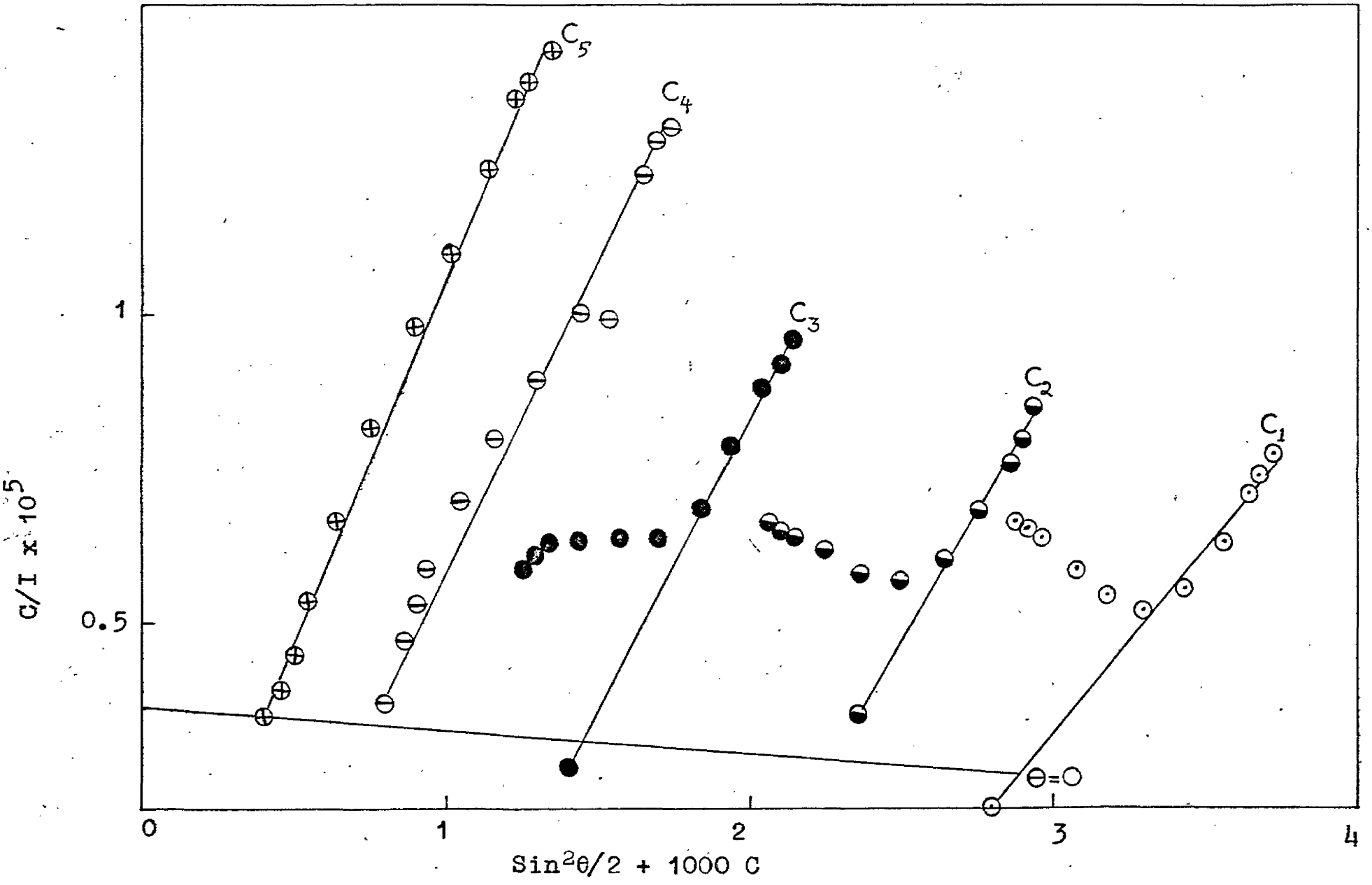
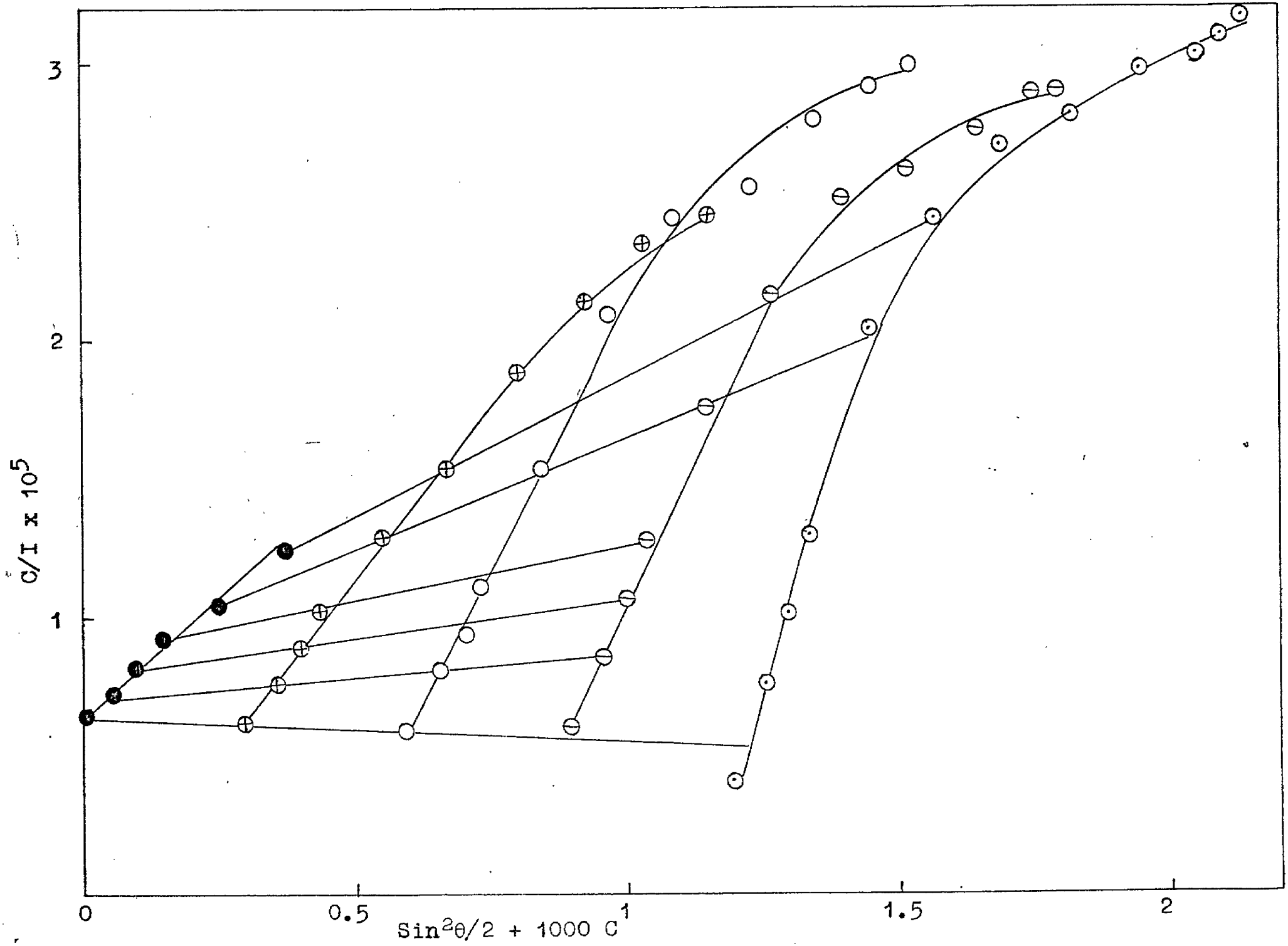



Fig. 56. Zimm plot for PVC Fraction $b_1$ degraded 210 minutes at 178° C


3
2
1
C/I x 10^5
0
0.5
1
1.5
2
Sin^2θ/2 + 1000 C^1

Degradation of polymer

The degradation of PVC was studied using precipitated polymer and first fraction of associated PVC ($b_1$) ($[\eta]$= 1.48 dl. gm.$^{-1}$).

The Zimm plots become distorted after half an hour of degradation. The $c/I_s$ value at higher angles continues to increase but at lower angles (below 90°) a reverse behaviour takes place. The $c/I_s$ value for 30° and other angles is higher than for 90°, and consequently a very twisted Zimm plot is produced. The extrapolation for  = 0 and C=0 line was done using the value obtained at angles above 90°. This type of extrapolation is open to criticism, but similar sort of extrapolation has been used by Spitsbergen and Beachell[101] for oxidised polystyrene. It is very difficult to assign any specific reason for the distortion of Zimm plot. If it were due to microgel or cross-linked PVC, the value of $c/I_s$ would have decreased markedly at lower angles. Another possibility may be that other changes taking place in the polymer chain are responsible for this distortion. It was observed that the distortion was removed when the centrifugation of solution was done after 24 or 48 hrs. of degradation. The solutions were kept at room temperature in volumetric flasks with glass stoppers. This phenomenon is best illustrated in Fig. 56 and 57, where in one case the centrifugation and recordings were taken immediately after degradation while in other case

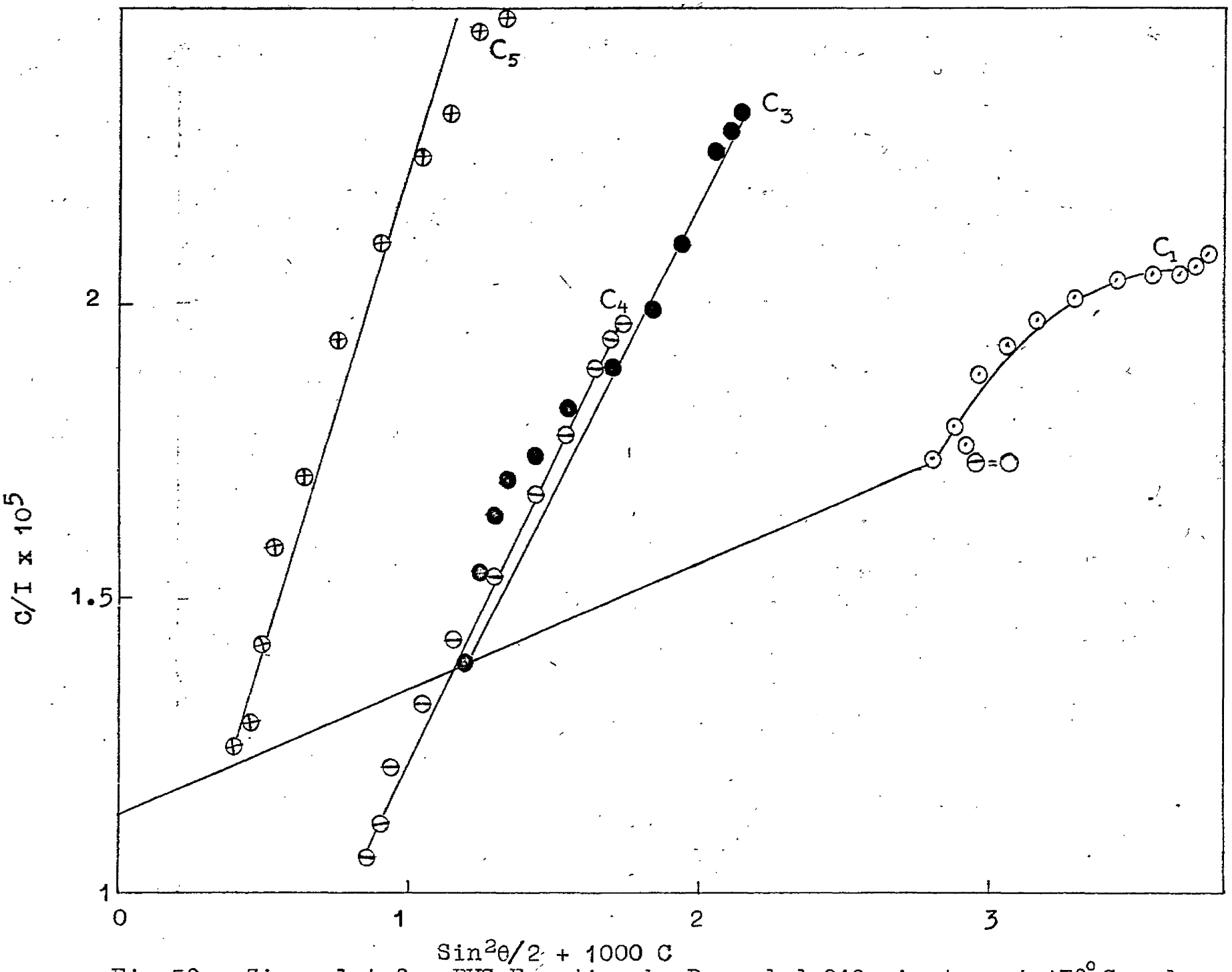



Fig.58. Zimm plot for PVC Fraction $b_1$ Degraded 210 minutes at 178°C and subsequently oxidised.

the centrifuge was done 48 hours after degradation. Similar removal of distortion was also observed in 1st fraction of PVC ($b_1$) degraded 2½ hours at 178°C. The polyene chain produced on degradation may react with oxygen when the solution is kept at room temperature for long time. A subsequent chain scission may take place, and perhaps this breaking of chain is responsible for the removal of distortion. This implies that long polyene chains produced on degradation are responsible for distortion of Zimm plots. To verify this point oxygen was passed for one hour in 3½ hrs. degraded PVC (fig. 56) in each solution at room temperature. The solutions were then centrifuged again and light scattering measurements performed on them. The result is plotted in fig. 58. The upside curvature at lower angles is removed by this treatment. However, this deliberate oxidation or keeping the solution in air causes a decrease in molecular weight. The $\bar{M}_w$ for 3½ hrs. degraded $b_1$, when measurements were done immediately after degradation, was 1,760,000, after passing oxygen into the solution the value dropped to 568,000. Leaving the solution degraded 3½ hrs. at room temperature for 48 hrs. gave a value of 1,010,000 for the molecular weight. Thus undistorted Zimm plots can only be obtained at the expense of lowering of molecular weight (which means chain scission).

In the following table the value of $\bar{M}_w$ for the various degradation times are mentioned.

Table 25

The degradation of PVC at 178°C in cyclohexanone

| Degradation time (in mins.) | $\bar{M}_w$ precipitated PVC | $b_1$ | Centrifugation done after precipitated PVC | $b_1$ |
|---|---|---|---|---|
| 0 | 165,000 | 804,000 | - | - |
| 10 | 124,000 | 334,000 | immediately | 24 hrs. |
| 30 | 123,000 | 578,000 | immediately | 24 hrs. |
| 60 | 315,000 | - | immediately | - |
| 90 | - | 948,000 | immediately | - |
| 150 | 641,000 | 1135,000 | immediately | 48 hrs. |
| 210 | - | 1770,000 | immediately | - |

Thus an initial decrease in molecular weight takes place for precipitated PVC as well as the $b_1$ sample. The significant decrease in $\bar{M}_w$ for $b_1$ in first 10 minutes may be due to disintegration of microgel. There is a decrease in $\bar{M}_w$ for precipitated PVC, even if one assumes a 10% experimental error. Thus chain scission had taken place slightly during this thirty minutes heat treatment of PVC. Later on, as heating time is increased the molecular weight for both precipitated PVC and $b_1$ increase. After 150 mins. of degradation the value is roughly four times the initial value (here it is assumed that value of $\bar{M}_w$ obtained after 10 minutes of degradation of $b_1$ is the correct figure).

Due to the distortion of Zimm plots the number average molecular weights could not be calculated at later stages of

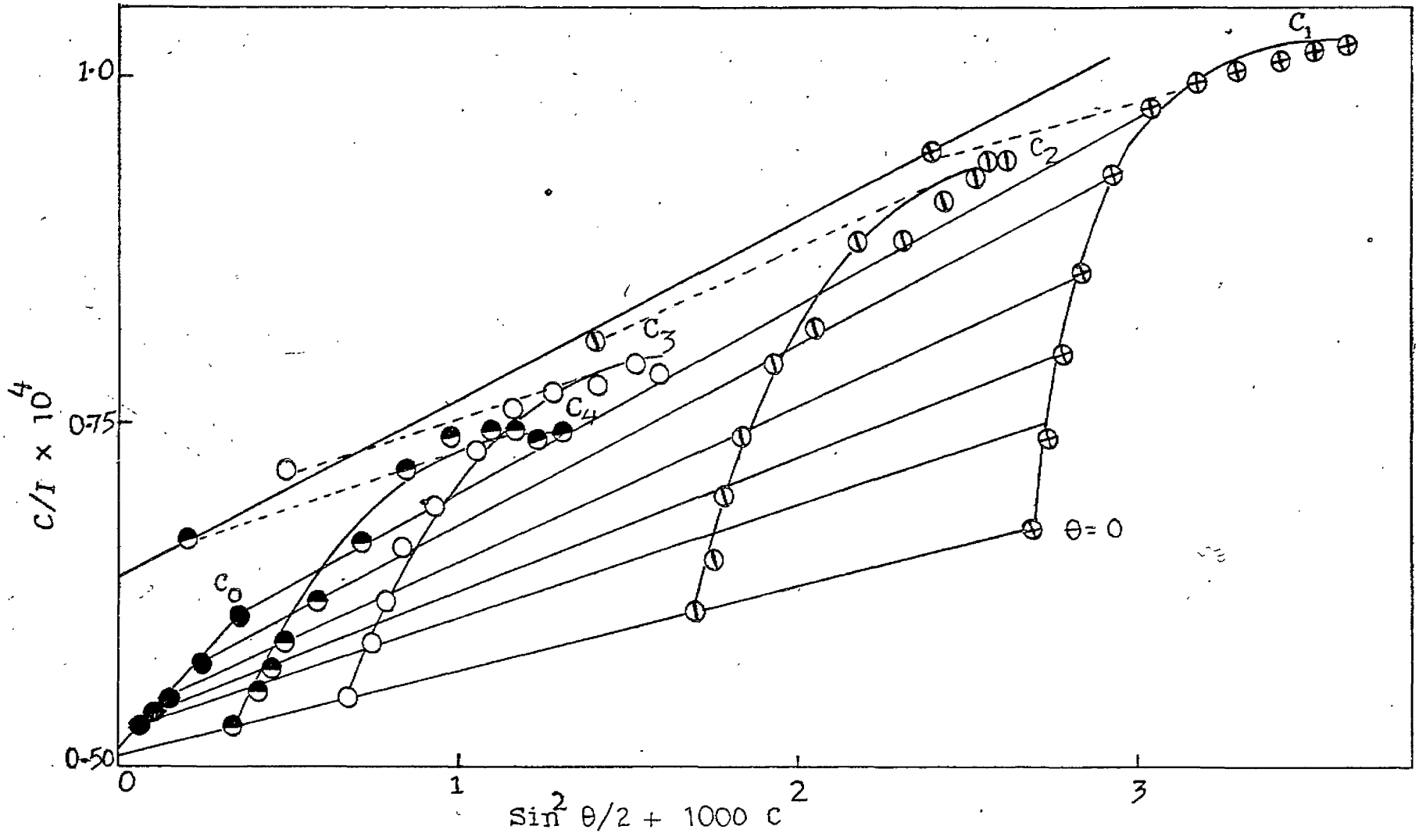



Fig. 59 Zimm plot for PVC (precipitated ) degraded for 10 minutes at 178° C in cyclohexanone.

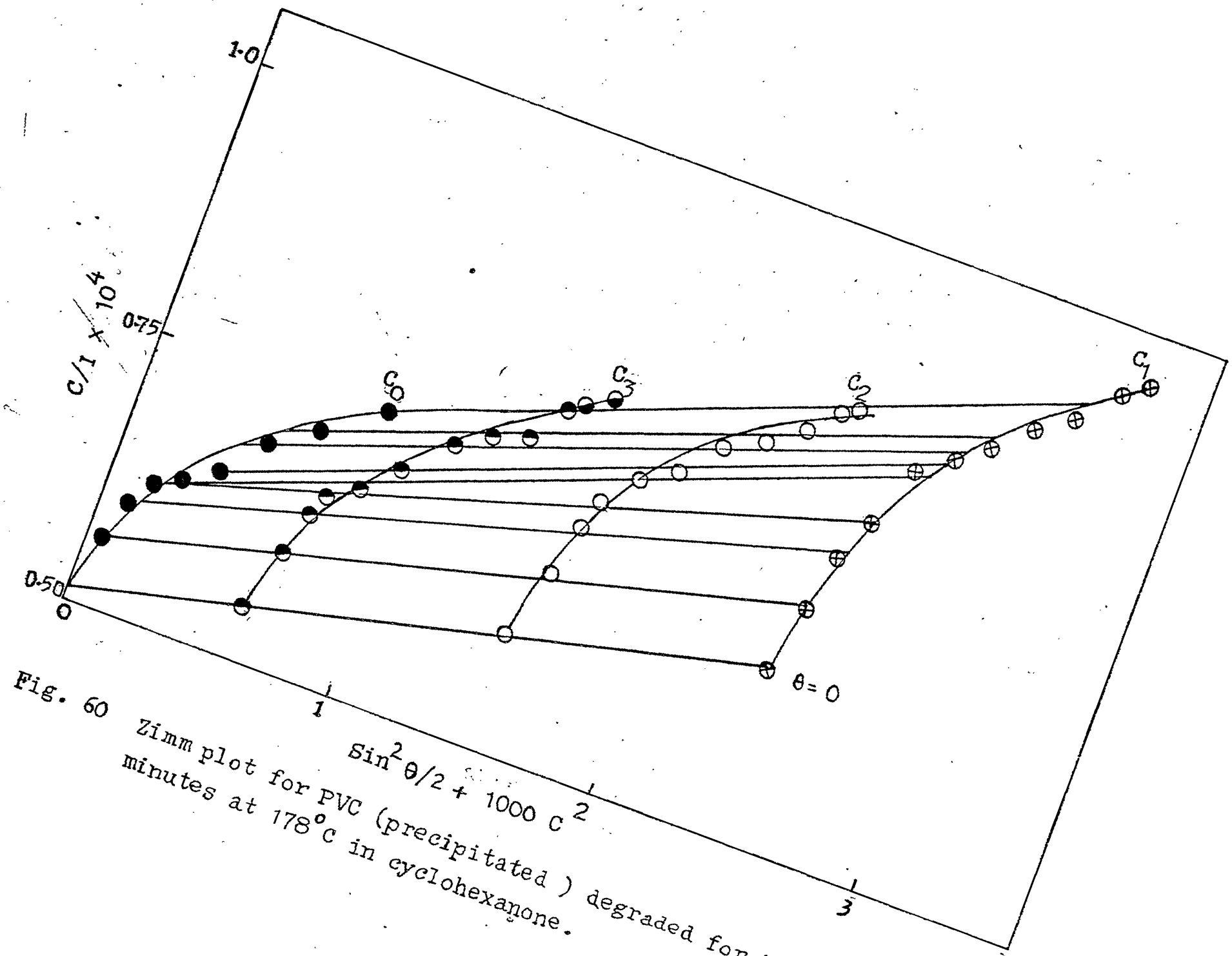



Fig. 60 Zimm plot for PVC (precipitated ) degraded for 30 minutes at 178°C in cyclohexanone.

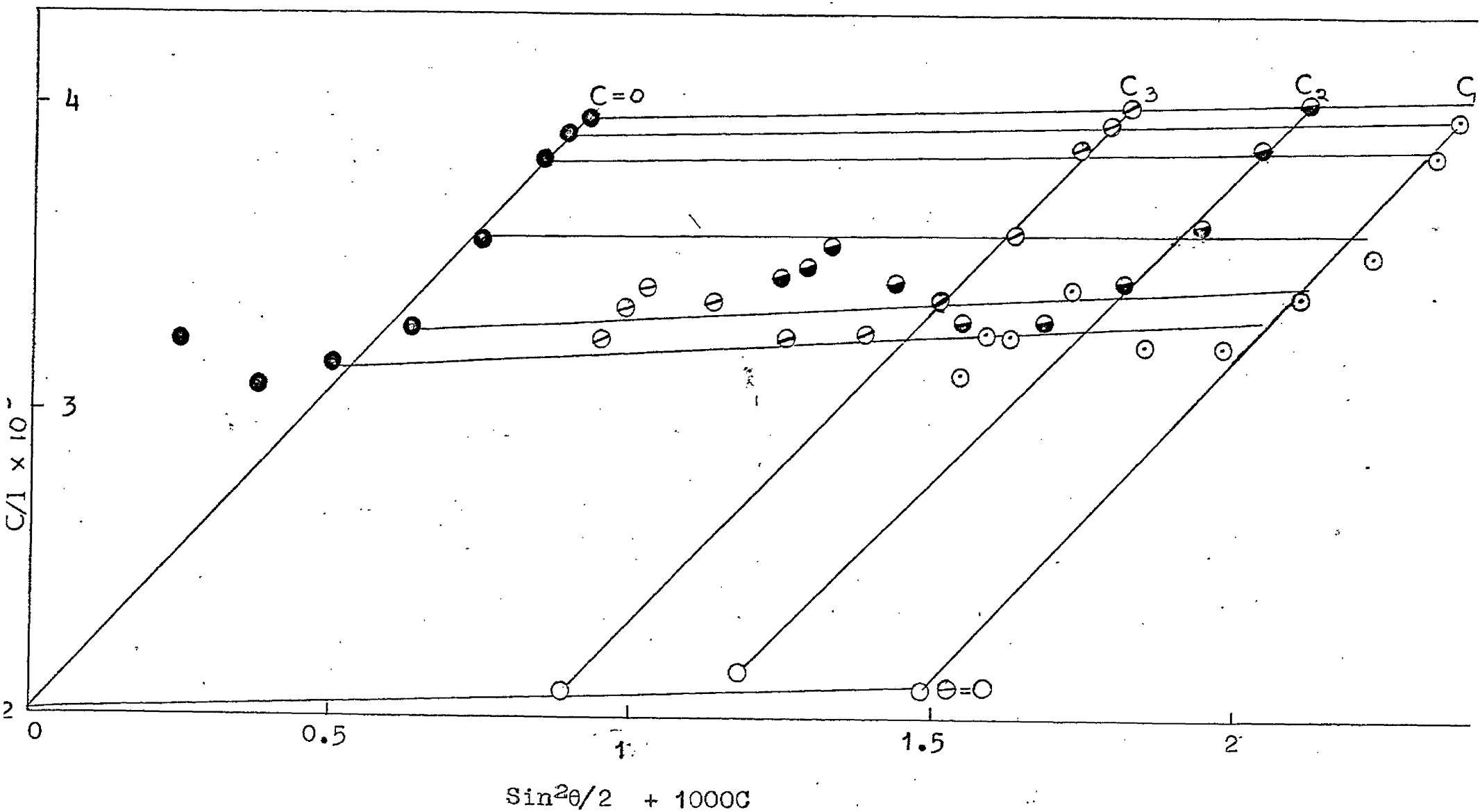


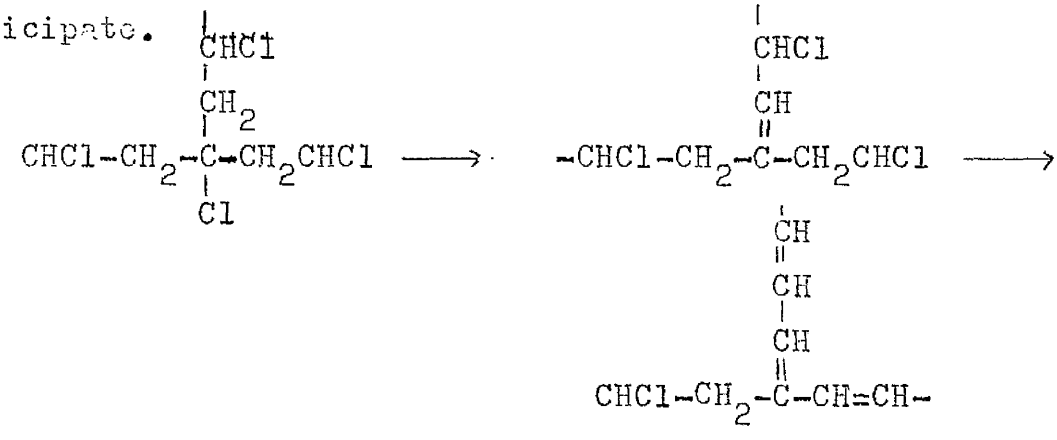

Fig. 61. Zimm plot for PVC (Precipitated polymer) degraded to 60 minutes at 178° C in Cyclohexanone showing distortion of angular scattering diagram.

degradation. For the first 10 and 30 minutes of degradation (fig. 59 and 60) the value of $\bar{M}_n$ for precipitated PVC was 50,000 and 51000 respectively. The value for undegraded PVC was 59,000. This variation in the $\bar{M}_n$ values is within the limits of experimental error. The $\bar{M}_w/\bar{M}_n$ ratio for undegraded 10 minutes and 30 minutes degraded PVC is 2.77, 2.46 and 2.407. This indicates a slight decrease in polydispersity of the polymer for first 30 minutes of degradation. A narrowing of molecular weight distribution is to be expected in these polymers where chain scission is the main reaction as in oxidation of polystyrene[32]. The $\bar{M}_n$ for the 10 mins. and the 30 mins. degraded first fraction of pplymer had the value of 104,000 and 84,000 repsectively and the $\bar{M}_w/\bar{M}_n$ ratio would be 3.21 and 6.9.

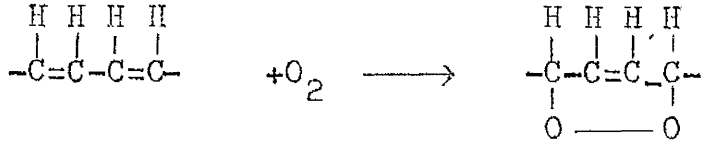
Due to the distortion of Zimm plots the second virial coefficients and radius of gyration were not calculated. The slope of $\theta = 0$ line becomes negative as the degradation proceeds beyond 30 minutes (fig. 56 ). This type of negative slope has been reported for polyelectrolytes in salt solutions.

The marked decrease in molecular weight on oxidation of the 3½ hrs. degraded sample suggest chain scission. The 150 mins. heated sample of precipitated PVC on keeping at room temperature for 14 hrs. showed a decrease in molecular weight from 642,000 to 538,000. This type of chain scission indicates that oxidation of polyene inside the polymer chains had taken

place. It is generally believed that degradation starts at the double bonds situated at the chain ends, tertiary chlorine atoms present in the polymer chain may also act as a secondary source of initiators. Baum and Wartman[11] have shown by ozonolysis studies that the double bonds are the main initiators of dehydrochlorination but later on tertiary chlorides also participate.



Thus dehydrochlorination can proceed in three directions simultaneously. If a polyene chain of this type is oxidised, the subsequent chain scission would cause a marked decrease in molecular weight, whereas if a polyene chain situated at the end of polymer chain is oxidised, the effect on $\bar{M}_w$ would not be so significant. Peroxide and hydroperoxides are formed initially by the reaction of $O_2$ with conjugated double bonds which break



down and thus cause chain scission. Our result suggests that tertiary chlorides also participate in the degradation of PVC.

Fig.62 Schlieren photographs of PVC showing slow rate of sedimentation in cyclohexanone conc. = 0.69 g.100ml$^{-1}$, Photo interval = first photo after 96 minutes, 16 minutes interval between the other photographs.

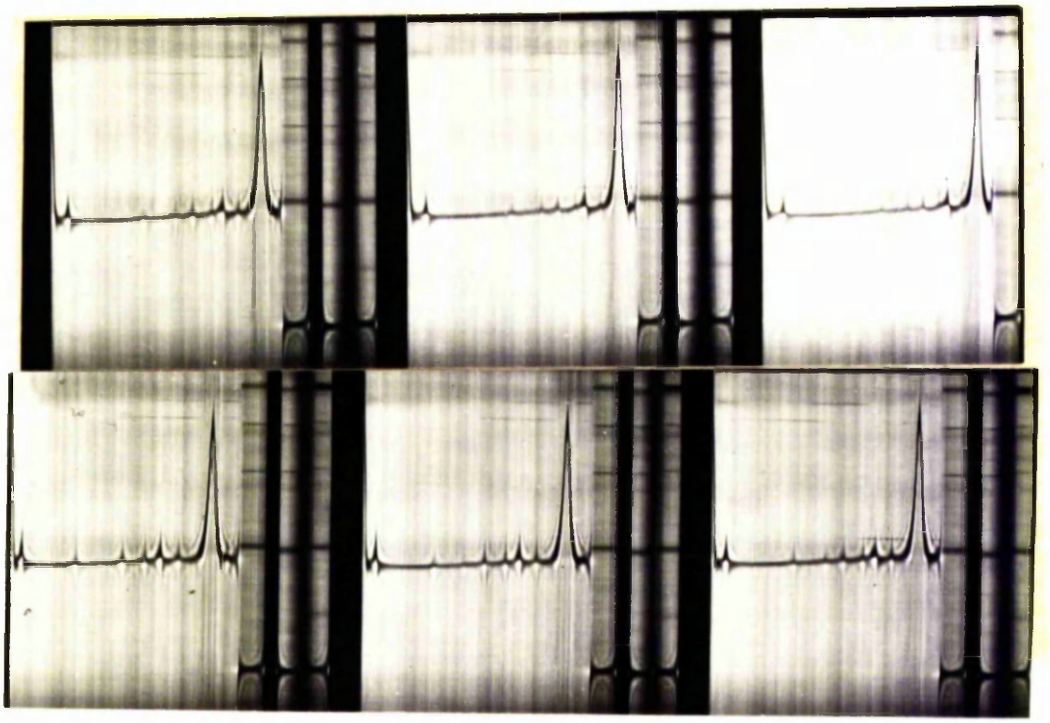
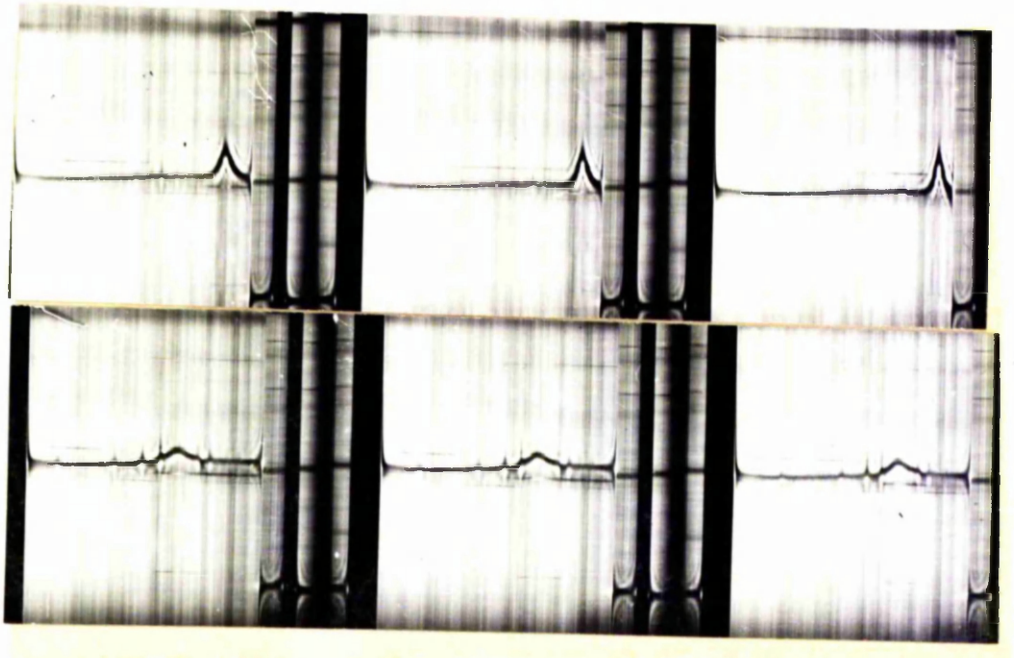


Fig.63 Schlieren photographs of PVC at low concentration. (o.15 g.100ml$^{-1}$,) Photo interval = 4 mins. between 3 & 4 = 24 mins.



Ultracentrifuge measurements

The first fraction of associated PVC ($b_1$) was selected for the degradation studies using the ultracentrifuge. The reasons for selecting this particular fraction were two fold (1) to determine whether the associated polymer is stable at such a high temperature (178°C) as used in degradation and (2) because it would be more homogeneous than the whole polymer, where several tiny peaks representing different molecular weight species make their appearance about 60 mins. after the start of centrifugation, and the major peak itself does not remain symmetrical (see fig. 51 and 54). It was found that rate of sedimentation in cyclohexanone was very slow (fig. 62). This may be due to the high viscosity of polymer solution in cyclohexanone. It was, therefore, decided to use tetrahydrofuran as a solvent in subsequent studies.

The sedimentation coefficient (Sc) at four different concentrations was first determined and from this the sedimentation constant for this fraction was calculated. At the high concentration of polymer (0.59 or 0.69 gm. 100 ml.$^{-1}$) only one major peak with a tiny fast sedimenting peak (representing associated PVC) appear initially. Later on after about 80 minutes of start of ultracentrifuge, few very tiny peaks started to appear. This may be due to the polydispersity of this fraction. However, the major peak remained symmetrical throughout (fig. 54). This

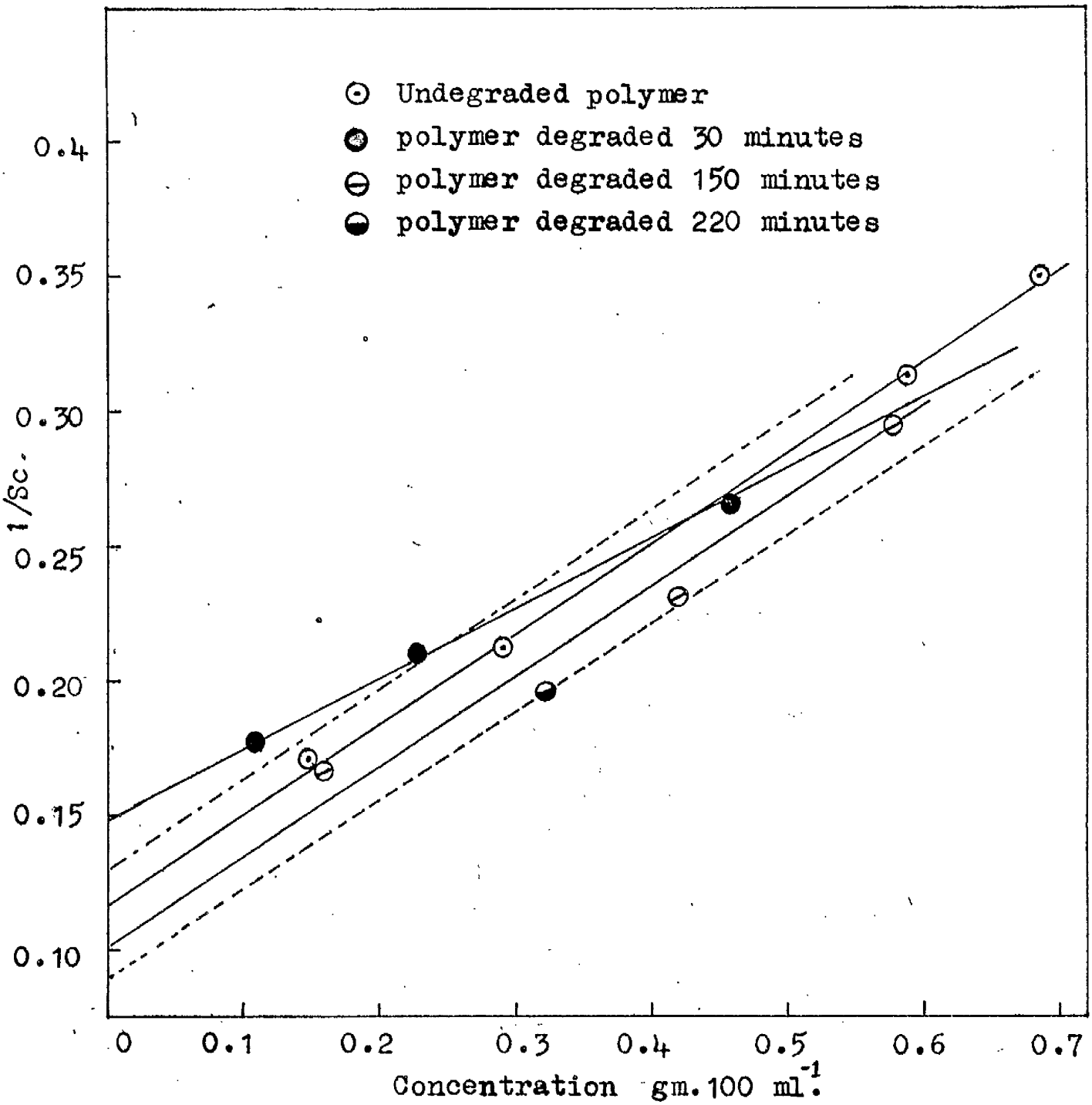
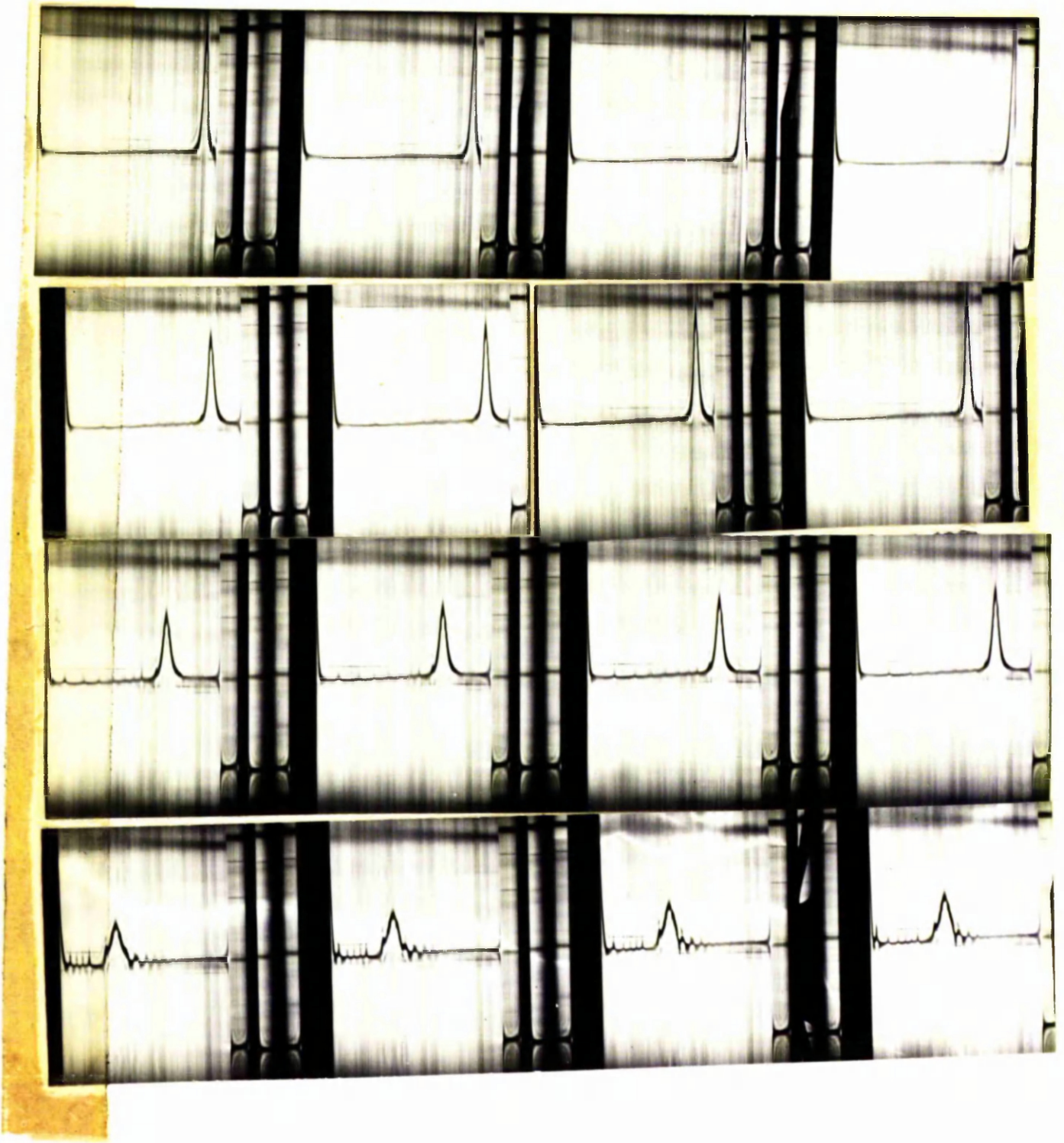



Fig. 64 Evaluation of sedimentation constant for degraded and undegraded PVC ( fraction $b_1$).

Fig.65 Ultracentrifuge photographs for PVC degraded 30 minutes at 178 °C, conc. = 0.4597 g.100ml$^{-1}$, solvent = THF.

Photo interval = 4 minutes for first six photo graphs, 8 minutes later on, there is a difference of 48 minutes in between 12 and 13 photo.



phenomenon is more pronounced at lower concentration (0.2963 or 0.1481 gm. 100 ml.$^{-1}$) when the major peak becomes very much diffused later on (fig. 63). The plot of 1/Sc against concentration (fig. 64) gave a value of 8.69 Svedberg for the sedimentation constant for this fraction.

The degradation studies were carried on by degrading the polymer in cyclohexanone for required time in a sealed tube. The tube and its contents were cooled to the room temperature, before being opened. The polymer was precipitated by adding it to excess of methanol with constant stirring. The solution was filtered, and the polymer was dried for 24 hrs. on the vacuum line. A known weight of this polymer was dissolved in freshly distilled tetrahydrofuran and used for sedimentation measurements. The determination of Sc at different concentrations was done by diluting a known volume of this standard solution with appropriate amounts of freshly distilled THF.

The effect of degrading the polymer for 30 minutes at 178$^{o}$C was the complete disappearance of the tiny peak representing microgel. This means that the microgel is not stable at this temperature and disintegrates completely (fig. 65). There was no other significant difference in the sedimentation diagrams. The appearance of only few tiny peaks between major peak and meniscus can not be regarded as a conclusive proof of the presence of low molecular weight polymer. The low molecular weight

Fig. 66 Schlieren photographs of PVC degraded 150 minutes at 178°C in cyclohexanone. Solvent= THF, Conc. =0.4142 g.100 ml.$^{-1}$ Photographic interval= 4 minutes. First photo after 12 mins. of start, and the time difference between 3-4 and 6-7 is 12 minutes.

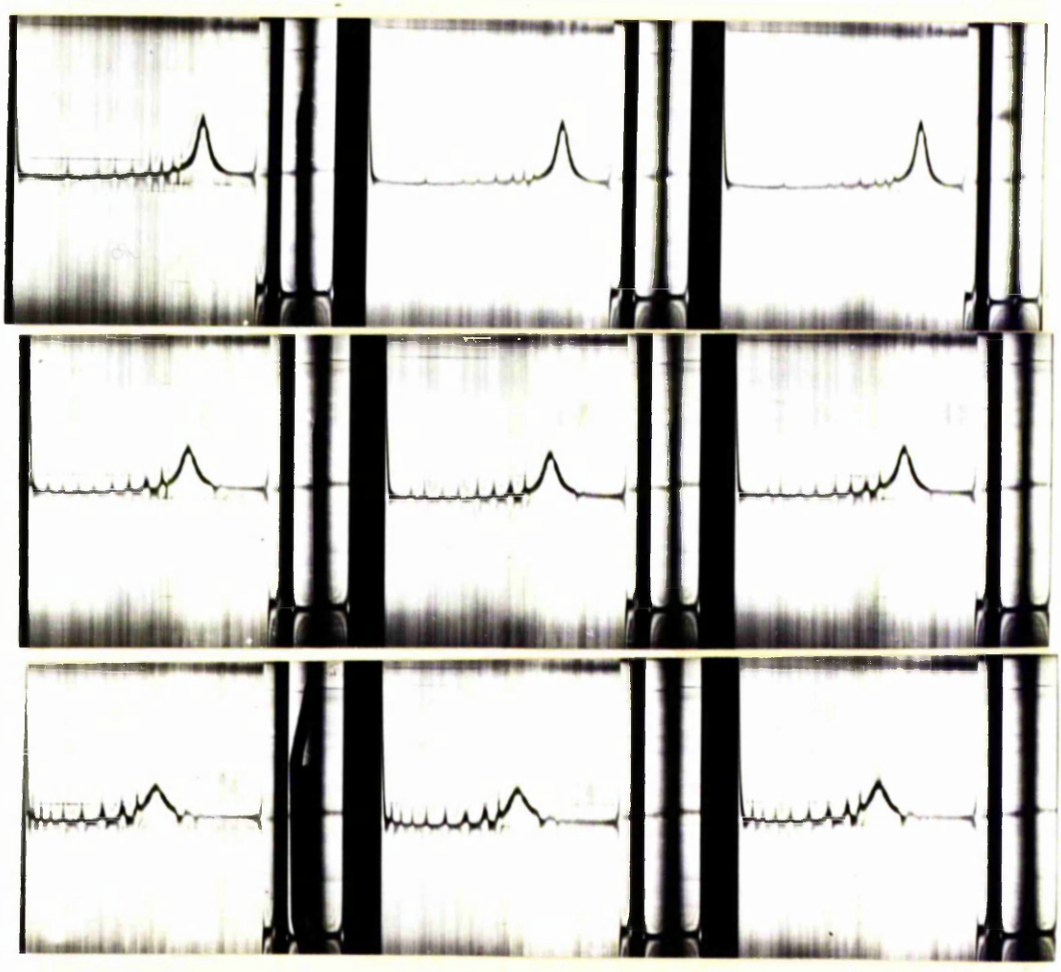
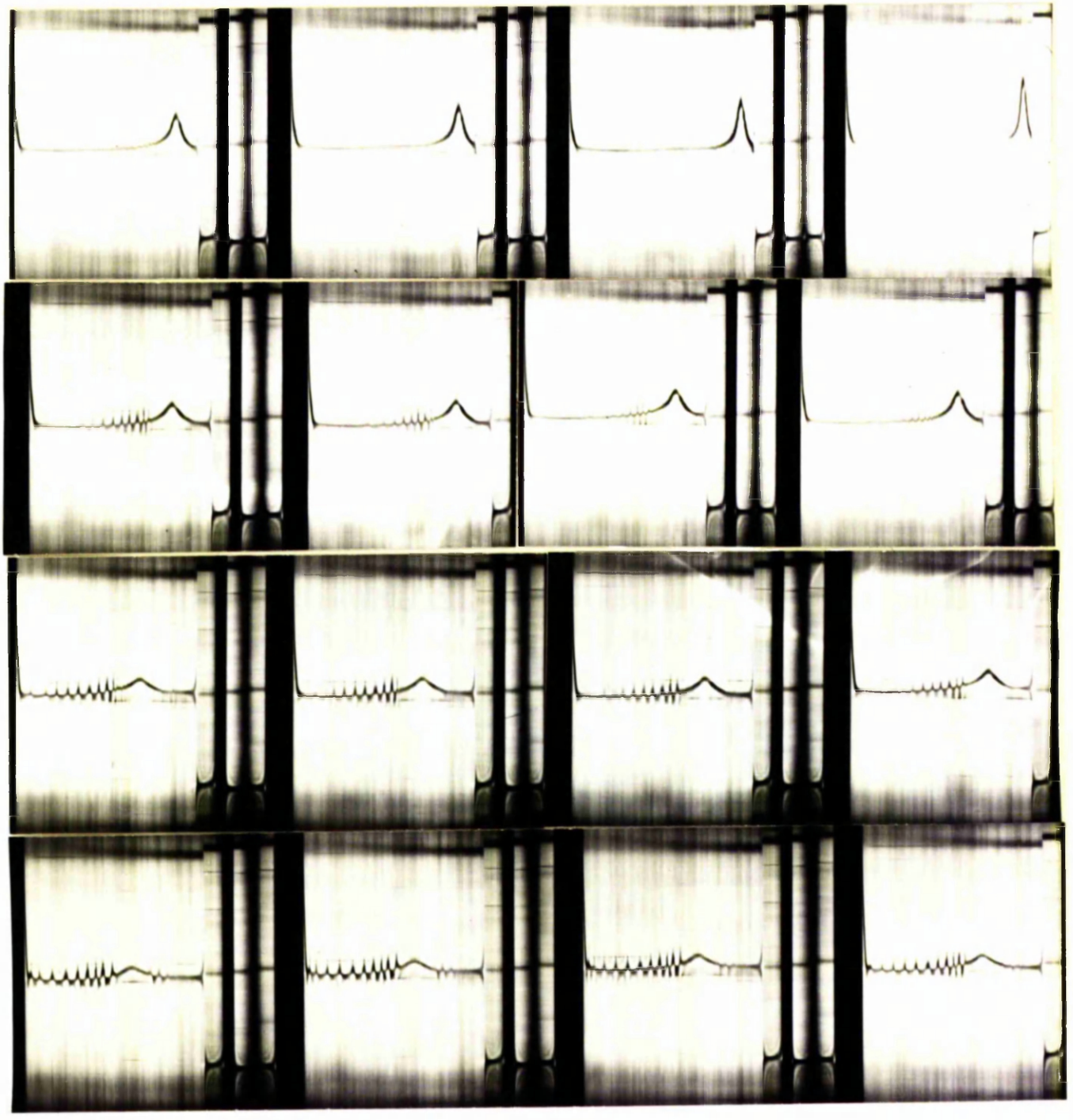


Fig.67 Schlieren photographs of PVC degraded 220 minutes at 178°C in cyclohexanone conc. = 0.3240 g.100ml$^{-1}$, solvent = THF, photo interval = 4 minutes.



polymer could easily be lost during precipitation. There can be two possible values of sedimentation constant 6.66 Svedberg or 7.61 Svedberg. If the former value is taken as correct it would mean a change of the slope of the 1/Sc Vs concentration line, which is difficult to explain. Both the values, however, indicate a lowering of sedimentation constant, which indicates a decrease in the molecular weight of the sedimenting sample.

It was then decided to degrade the polymer for a long time i.e. 150 mins. and 220 mins. The sedimentation diagrams of this polymer showed the appearance of several distinct tiny peaks after 22 mins. of the start of centrifuge (see fig. 66 and 67). The number of these peaks gradually increased with time, some of them split into two at later stages of sedimentation. For 150 mins. degraded sample the sedimentation constant was 10 svedbergs. Sedimentation coefficient was measured only at one concentration for 220 minutes degraded polymer. The sedimentation constant for this gave a value of 11.11 svedberg.

Sedimentation coefficients for the first 5 or 6 tiny peaks were also determined. These are tabulated in the following table. The peaks were numbered in reverse order i.e. the peak making appearance first was numbered as $P_6$ and so on.

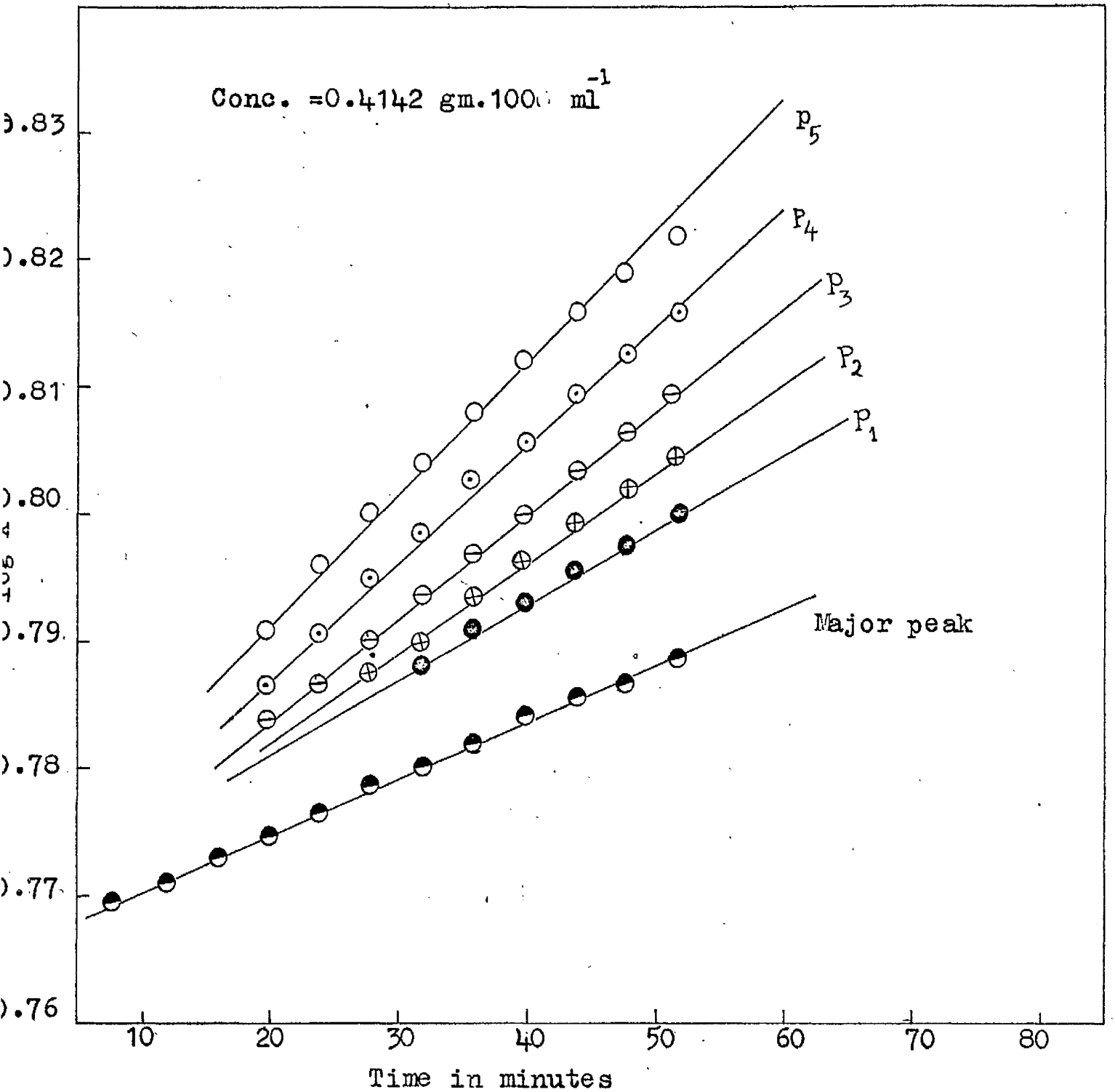



Fig. 68 Sedimentation coefficient determination of major peak and some minor peaks for PVC degraded 150 minutes.

Table 26

Sedimentation coefficients of different peaks observed on degradation of PVC fractions $b_1$

| Polymer sample | concentration g./100 ml. | Sedimentation coefficients (svedbergs) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $P_1$ | $P_2$ | $P_3$ | $P_4$ | $P_5$ | $P_6$ |
| 150 mins. | 0.4142 | 5.7457 | 6.9178 | 7.9870 | 9.1434 | 10.1763 | |
| 220 mins. | 0.3240 | 9.1993 | 10.0794 | 10.9760 | 12.3186 | 13.230 | 14.70 |

However, one can never be sure that certain peak appearing at any one particular position would be the same for both 150 mins. run and 220 mins. run. So the two data cannot be compared. One can only say that the first tiny peak appearing at 150 mins. degradation time sedimented 2.3 times faster than the major peak while at 220 mins. it was 2.9 times faster than the major peak.

The results of ultracentrifuge thus indicate a chain scission at initial stages of degradation. But as the degradation time increases on increase in Sc and consequently in molecular weighttakes place. The experiments using light scattering measurements also indicated an increase in molecular weight when polymer is degraded for a long time.

# CHAPTER 6

## General Discussion

Before going into a detailed discussion, it would be better to evaluate the errors involved in the various methods used in this thesis.

Absorption studies It has already been pointed out that polyene chains are susceptible to oxidation. This factor makes the measurements in the ultraviolet region difficult, because such measurements could not be carried under vacuum. It was necessary to precipitate the polymer, (because of the strong absorption of the high boiling solvents), and thus the polymer was in contact with air for some time.

Our results indicated that the absorption at 215 m $\mu$ was the maximum, which would indicate the predominant existence of a two double bonds conjugated species i.e. of butadiene type. However, this could also arise as a result of oxidation of longer polyene chains. Single C=C double bonds could not be estimated in our u.v. studies because they absorb at too low a wavelength.

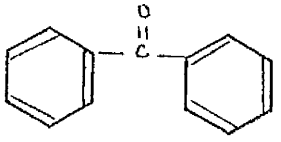
Light scattering measurements Light scattering is regarded as an absolute method of determining molecular weights. The value obtained for the molecular weight, however, could be altered considerably depending upon the extrapolation. Such extrapolations are a bit more difficult in our experiments, because

the Zimm plots were markedly curved. Thus the Zimm plot shown in fig. 48 could be extrapolated to give an intercept of 2.3 x $10^{-5}$ (as obtained) or 2.35 x $10^{-5}$ or 2.45 x $10^{-5}$. This would cause a change in the molecular weight from 279,000 to 295,000 or 265,000. An error of $\pm$ 10% is thus easily incurred depending upon the way one carries out the extrapolation.

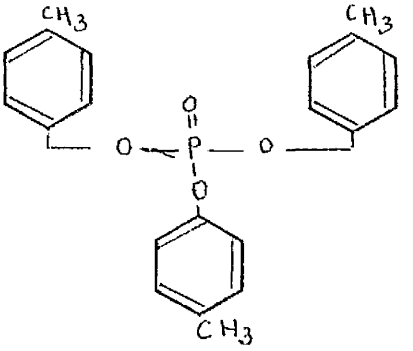
These variations in the slopes of the zero concentration and the zero angle lines would also be reflected in the values of the radius of gyration and of the second virial coefficients. These parameters, can thus be measured only with considerable error.

Dehydrochlorination in solution

Solvents influence the dehydrochlorination of PVC and the rate of dehydrochlorination varied from solvent to solvent. The rate was fairly low in chlorinated hydrocarbon solvents (as dichloronaphthalene) and high in benzophenone and tritoluylphosphate. Solvents having a C=O group or other active ether groups (as tritoluylphosphate) appear to facilitate the dehydrochlorination

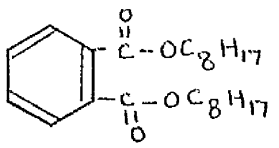


benzophenone



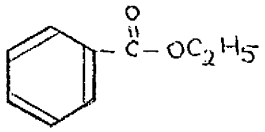
tritoluylphosphate

However, it is difficult to make any generalisations, because in ethylbenzoate and in dioctylphthalate PVC degrades at a slower rate than in benzophenone



dioctylphthalate

or



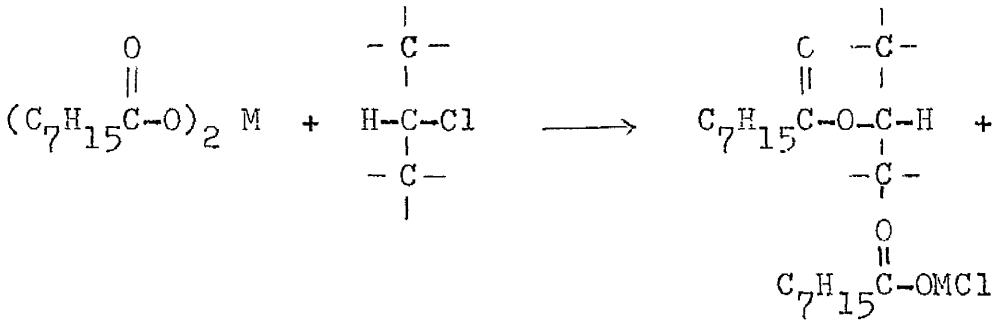
ethylbenzoate

It has been suggested[65] that the alcohol grouping of the ester has some influence on dehydrochlorination. The shorter the chain length of the substituent attached to nucleus, the greater is the degree of chain scission in the degradation of the polymer.

An attempt was also made to correlate the variation in rate with the dielectric constants of the various solvents. No systematic variation in the rate with dielectric constants was observed, and perhaps this does not influence the dehydrochlorination. The dielectric constant of the medium normally affects the rate of ionic reactions. Thus the dehydrochlorination of PVC is probably not an ionic reaction. This may indicate that solvation (solvent-solute interaction) has got some influence on dehydrochlorination. However, it is difficult to conceive a difference in the solvating power of say tritoluyl-phosphate and dioctylphthalate.

Another possibility is the existence of an ester interchange

reaction between labile chlorine groups in the polymer molecules and the solvents. Such reactions are known to occur with salts, but have not been reported for esters in the absence of catalysts.



Bengough et. al have investigated this type of interchange reactions with PVC and metal carboxylates.

If such interchange reactions with solvent and polymer take place, then it may be said that the structures produced after interchange exert some influence on the dehydrochlorination of PVC.

Effect of molecular weight on dehydrochlorination and discolouration of PVC

Our investigations with PVC fractions indicate that the rate of dehydrochlorination or increase in absorbance does not depend on the molecular weight of the polymer.

The high molecular weight fractions obtained by fractionation of commercial PVC may be expected to be more highly branched than the low molecular weight fractions of the same sample. This is because the polymerisation is carried to high conversion and

chain transfer reactions introducing branches ~~increase~~ become predominent at later stages of polymerisation. This is supported by our light scattering measurements. The intrinsic viscosity of $F_2$ is 1.32 dl.gm.$^{-1}$ which would give a molecular weight ($\bar{M}_w$) in the range of (117000 - 172000) but the observed value of 279,000 is considerably higher . This could be explained by branching, because the limiting viscosity does not increase to the same extent as $\bar{M}_w$ in case of branches polymer.

It has been mentioned in Chapter 4 that the number of end groups per structural unit of a branched molecule is considerably less than for an unbranches molecule. If, however, the branches are terminated by a chain transfer reaction with the monomer (which is believed to be the case) then the number of C=C bonds per structural unit would be equal for branched and unbranched polymer molecules.

$$\sim\sim\sim CH_2CHCl\cdot + CH_2{=}CHCl \longrightarrow \sim CH{=}CHCl + CH_3\dot{C}HCl \qquad (1)$$

This is because a linear polymer would be expected to have $CH_3CHCl-$ grouping at one end, which would not affect dehydrochlorination.

If chain termination is taking place by abstraction of a hydrogen atom from the monomer, then the number of C=C chain ends per structural unit would be higher for a linear polymer, than for a branched polymer.

$$\sim\sim\sim CH_2CHCl\cdot + CH_2{=}CHCl \longrightarrow CH_2CH_2Cl + CH_2{=}\dot{C}Cl \qquad (2)$$

This type of reactions are not favoured energetically because abstraction of a proton from a double bond is difficult.

On the other hand, if disproportionation is the main chain terminating process then

$$\sim\sim\sim CH_2CHCl + ClCHCH_2\sim\sim \longrightarrow \sim\sim CH{=}CHCl + ClCH_2CH_2\sim\sim\sim \qquad (3)$$

there is an equal probability of the formation of C=C groups at the chain ends of branches as of $-CH_2CH_2Cl$ group.

Out of these three chain terminating reactions, reaction (1) is believed to be the most important. According to this mechanism the number of double bonds situated at chain ends of polymer per structural unit, whether linear or branched would be equal. There is one other aspect which should not be overlooked. The polymerisation is initiated by catalysts. These would constitute one chain end per sinetic chain for both linear and branched molecule and initiation of dehydrochlorination may well take place from here. Thus the catalyst fragment end groups per structural unit is greater in linear than in branched polymer.

The branches in the polymer may introduce a tertiary chloride type of structure ( $\sim\sim CH_2-\underset{\displaystyle CH_2}{\overset{\displaystyle Cl}{\underset{|}{\overset{|}{C}}}}-CH_2CHCl\sim\sim$ ) . These may also act as initiators for dehydrochlorination by loosing a chlorine atom. Baum and Wartman have suggested that tertiary chlorides may act

as secondary source of initiation. It is not necessary that all the branches would be introduced by a transfer of hydrogen attached to chlorine and the possibility of the existence of branches of ($\sim CH_2CHClCH(\zeta)-CHClCH_2\sim$) this type could not be overlooked.

Thus, from our dehydrochlorination and absorption spectra studies it may be said that whatever excess of double bonds are present in low molecular weight polymer, they are compensated by the existence of tertiary chlorides in branched polymer.

The effect of chain ends could possibly be best investigated by taking a linear polymer of different molecular weights. Bengough and Sharpe[9] have studied the dehydrochlorination studies of polymer prepared at different temperatures by taking the polymerisation to low conversion. Branching is introduced at high temperature, but since the polymerisation was carried to low conversion, branches would be present in insignificant amounts. Their kinetic studies revealed that the rate of dehydrochlorination varied inversely with the degree of polymerisation.

Association of PVC The association of PVC in a few of the fractions of PVC has been reported in the thesis. Thus the mode of precipitation of the polymer requires considerable attention. The effect of associated PVC on rate of dehydrochlorination is insignificant (Chapter 3) but such microgel may affect the rate of cross linking. Though there is evidence that these microgels are disintegrated at higher temperatures (Chapter 5) the possibility of the existence

of few associated PVC molecules can not be overlooked. It was observed that gel points in some cases were not reproducible. This may well be due to the presence of the microgel in the polymer, which was always freed from peroxide catalyst etc., by precipitation. The gel point measurements have not been reported in the thesis, because only a few experiments were performed and these were not reproducible.

In the investigations of gel point, therefore, one should be sure of the absence of associated PVC. An initial run of polymer solution in the ultracentrifuge, can easily sort out this problem.

The influence of association on the molecular weight of PVC has been shown in Chapter 5.

Absorption studies Such measurements revealed that conjugated polyenes having a maximum of 13 double bonds are produced in degradation, though the majority of polyenes have fewer number of double bonds (2,3,4,5 or 6). The influence of temperature was manifested by a decrease in absorptionsat higher wavelengths. This is perhaps due to the cyclisation of chain ends of polyenes to produce six membered or higher rings, with a subsequent scission from the main chain. Such reactions have been reported by Stromberg[20] at higher temperatures (300°C).

The existence of chain scission reactions has been indicated by the molecular weight measurements using the light scattering

technique. There was a decrease in molecular weight from 160,000 to 124,000 on heating the polymer for 30 minutes at 178°C in cyclohexanone. However, the chain scission of higher polyenes at 198°C generally starts after 20 or 30 minutes of degradation. Whether this initial decrease in the molecular weight is due to dissociation of traces of associated molecules (not indicated in Schlieren diagram) or due to splitting of polymer chain at some weak points or due to cyclisation of polyenes is difficult to decide.

Possible mechanism for dehydrochlorination

Any mechanism for dehydrochlorination must take account of the following two facts.

(1) the high absorption in the ultraviolet region, indicating the existence of 2,3 or 4 double bond species in abundance over the long conjugated polyenes.

(2) the increase in absorption on keeping the degraded solution in vacuum at room temperature.

The first point could be accounted for if we envisage dehydrochlorination as a stepwise reaction and not a zipper reaction. It could be imagined that an initial production of a two double bonds structure takes place, which then eliminates another molecule of HCl to yield three double bonds and so on. This type of gradual build up in length of polyene chain also accounts for the previous

observation of Bengough and Sharpe[9]. These authors observed that the dehydrochlorination was not markedly influenced by free radical initiators, and from this they have concluded that propagation also requires an activation energy similar to initiation. This would not have been the case, if, dehydrochlorination was a 'zipper' reaction.

In the latter case, one would have expected to get a high absorption at longer wavelengths instead of at lower wavelengths.

The increase in the absorption on storage of a degraded solution, could be explained by the existence of free radicals of low reactivity. The existence of free chlorine atoms or other chain carriers is not supported by our work on the degradation in presence of monomers.

All these facts could be taken into account if one assumes the dehydrochlorination proceeds by the following mechanism.

Initiation The splitting of a chlorine atom under the influence of heat may be regarded as an initial step in the dehydrochlorination.

$$CHCl{=}CHCHClCH_2\sim\sim \longrightarrow CHCl{=}C\dot{H}CHCH_2\sim\sim + Cl\cdot$$

This free chlorine atom may either react with the solvent or it can initiate the dehydrochlorination in another polyene chain by abstracting hydrogen atom.

$$Cl\cdot + \sim\sim CH_2CHCl\sim\sim \longrightarrow \sim\sim\dot{C}HCHCl\sim\sim + HCl$$

These free chlorine atoms would be thus present only in negligible amounts at any time.

Propagation The propagation does not involve the free chlorine atoms, and the activating influence of free radicals is enough to

cause liberation of HCl.

$$CHCl{=}CH\dot{C}HCH_2CHCl \longrightarrow CHCl{=}CH\dot{C}HCH{=}CHCH_2 + HCl$$

$$CHCl{=}CH\dot{C}HCH{=}CHCH_2 \rightleftharpoons CHCl{=}CHCH{=}CH\dot{C}HCH_2CHCl$$

Subsequent elimination of HCl thus takes place along the polyene chain. This mechanism is similar to the scheme proposed by Arkman[16] and Bengough.[9] In the radiolysis of PVC Miller[33] has suggested that free chlorine atoms may not exist as such and a simultaneous liberation of chlorine and hydrogen take place to form HCl.

Dehydrochlorination would thus gradually increase, and the reaction could be stopped if a) there are defects in polymer chain e.g. branches [ $\sim\!\sim CH{=}CH\dot{C}HCH_2\underset{\xi}{C}HCH_2\sim\!\sim$ ] or an occasional head to head, tail to tail configuration $\sim\!\sim CH{=}CHCHClCHClCH_2CH_2\sim\!\sim$ b) the two growing free radicals of low reactivity react with each other to form a cross link.

$$\left.\begin{array}{l} CHCl{=}CH(CH{=}CH)_n\dot{C}HCH_2 \\ + \\ CHCl{=}CH(CH{=}CH)_n\dot{C}HCH_2 \end{array}\right. \longrightarrow \begin{array}{l} CHCl{=}CH(CH{=}CH)_nCHCH_2\sim\!\sim \\ \quad\quad\quad\quad\quad\quad | \\ CHCl{=}CH(CH{=}CH)_nCHCH_2\sim\!\sim \end{array}$$

Reaction (b) would cause a removal of free radical. Reaction (a) would stop dehydrochlorination in the chain, but the free radical would be retained. This may initiate dehydrochlorination in another polymer chain by a transfer reaction.

## Future Work

It has been mentioned that solvents affect the dehydrochlorination of PVC, and a suggestion has been made that ketonic groups facilitate it. The work could be extended by using solvents having different functional groups.

The effect of conversion on polymer degradation could also be investigated. This could be achieved by preparing polymer and carrying the polymerisation to several different percentage conversions. The effect of branching would be prominent at higher conversions, and thus an insight into the mechanism of initiation could be obtained. Incidentally, a branched polymer having tertiary chlorine atoms can be prepared by the carrying the polymerisation in presence of $CH_2=C(Cl)(Br)$ and vinyl chloride. A copolymer of this $\sim CH_2CHClCH_2CHClCH_2\overset{\overset{Cl}{|}}{\underset{\underset{Br}{|}}{C}}-CH_2CHCl-$ type would be produced and the photolysis of this polymer in presence of VC would yield $CH_2CHClCH_2CHClCH_2\overset{\overset{Cl}{|}}{C}\cdot-CH_2CHCl$. The radical thus produced may attack a monomer thus starting a new chain reaction and a branched polymer having tertiary chlorides would result. The number of such branching could be estimated by labelling the chlorine with radioactive chlorine $CH_2=C(Cl^*)(Br)$. The final assay of radioactivity and bromine in polymer would give a measure of branching. The degradation of such polymer would indicate the role of tertiary chlorides on dehydrochlorination. The influence of branching -CH- could be investigated by copolymerising vinyl chloride and vinyl bromide. The subsequent photolysis of

copolymer $-CH_2CHClCH_2CHBrCH_2CHCl-$ would initiate other series of reaction in presence of monomer, and this would introduce branches attached to a carbon having a hydrogen atom.

It has been mentioned in the introduction that chain ends which may contain catalyst fragments may constitute a weak site for the initiation of dehydrochlorination. It would, therefore be interesting to use different catalysts for the initiation of polymerisation, and then carry out dehydrochlorination studies on the polymers formed.

The polymerisation of vinyl chloride may also be carried out in the presence of solvents. A chain transfer reaction with the solvent would introduce a different type of coiling in the polymer. The influence of solvents and group fragments could be evaluated by dehydrochlorination studies.

The stereoregularity of polymer may have some influence on dehydrochlorination, though at such a high temperatures as used in degradation, this effect may be insignificant. This possibility could, however, be explored by preparing syndiotactic polymer Syndiotactic crystalline PVC can be prepared by carrying the polymerisation at very low temperatures $-70^{\circ}C$. Thus Burleigh has reported that the absorbance ratio of 635/692 $cm.^{-1}$ (a measure for crystallinity) is 1.5 for PVC prepared by bulk polymerisation at $50^{\circ}C$. and 2.6 for that prepared at $-70^{\circ}C$.

Finally the work could also be extended by using the

ultracentrifuge and carrying the degradation very near to the gel point. Our experiments indicated the existence of several polymer species when polymer was degraded for 220 mins. However, the gel point was about at 280 mins. It would be interesting to know whether these different species increase in quantity (which would be manifested by the height of the peak) near the gel point or some other changes take place.

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